PESTICIDES MONITORING JOURNAL

DECEMBER 1979

VOLUME 13 NUMBER 3

PEMJAA (13) 81–135 (1979)

The *Pesticides Monitoring Journal* is published quarterly under the auspices of the Federal Working Group on Pest Management (responsible to the Council on Environmental Quality) and its Monitoring Panel as a source of information on pesticide levels relative to humans and their environment.

The Working Group is comprised of representatives of the U.S. Departments of Agriculture; Commerce; Defense; the Interior; Health, Education, and Welfare; State; Transportation; and Labor; and the Environmental Protection Agency.

The Monitoring Panel consists of representatives of the Agricultural Research Service, Animal and Plant Health Inspection Service, Extension Service, Forest Service, Department of Defense, Fish and Wildlife Service, Geological Survey, Food and Drug Administration, Environmental Protection Agency, National Marine Fisheries Service, National Science Foundation, and Tennessee Valley Authority.

The *Pesticides Monitoring Journal* is published by the Chemical Information Division, Office for Program Integration and Information, Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency.

Pesticide monitoring activities of the Federal Government, particularly in those agencies represented on the Monitoring Panel which participate in operation of the national pesticides monitoring network, are expected to be the principal sources of data and articles. However, pertinent data in summarized form, together with discussions, are invited from both Federal and non-Federal sources, including those associated with State and community monitoring programs, universities, hospitals, and nongovernmental research institutions, both domestic and foreign. Results of studies in which monitoring data play a major or minor role or serve as support for research investigation also are welcome; however, the Journal is not intended as a primary medium for the publication of basic research. Publication of scientific data, general information, trade names, and commercial sources in the *Pesticides Monitoring Journal* does not represent endorsement by any Federal agency.

Manuscripts received for publication are reviewed by an Editorial Advisory Board established by the Monitoring Panel. Authors are given the benefit of review comments prior to publication. For further information on Journal scope and manuscript preparation, see Information for Contributors at the back of this issue.

Editorial Advisory Board members are:

John R. Wessel, *Food and Drug Administration, Chairman*
Robert L. Williamson, *Animal and Plant Health Inspection Service*
Anne R. Yobs, *Center for Disease Control*
William F. Durham, *Environmental Protection Agency*
Gerald E. Walsh, *Environmental Protection Agency*
G. Bruce Wiersma, *Environmental Protection Agency*
William H. Stickel, *Fish and Wildlife Service*
Allan F. Isensee, *Science and Education Administration—Agricultural Research*
Herman R. Feltz, *Geological Survey*

Address correspondence to:

Paul Fuschini (TS-793)
Editorial Manager
Pesticides Monitoring Journal
U. S. Environmental Protection Agency
Washington, D.C. 20460

CONTENTS

Volume 13 December 1979 Number 3

Page

HUMANS

Sources of parathion exposures for Israeli aerial spray workers, 1977 ____ 81
Bension Cohen, Eliahu Richter, Eliahu Weisenberg, Judith Schoenberg, and Menachem Luria

FOOD AND FEED

Pesticides and other chemical residues in infant and toddler total diet samples—(I)—August 1974–July 1975 ____ 87
Roger D. Johnson, Dennis D. Manske, Dallas H. New, and David S. Podrebarac

FISH, WILDLIFE, AND ESTUARIES

Organochlorine pesticide residues in animals of Tasmania, Australia—1975–77 ____ 99
Harry Bloom, Walter Taylor, Walter R. Bloom, and Geoffrey M. Ayling

DDT in northern pike (Esox lucius) *from the Richelieu River, Québec, Canada, 1974–75* ____ 109
Serge Boileau, M. Baril, and J. G. Alary

Organochlorine residues in young herons from the upper Mississippi River—1976 ____ 115
Harry H. Ohlendorf, James B. Elder, Rey C. Stendell, Gary L. Hensler, and Richard Johnson

WATER

Herbicide contamination and decontamination of well waters in Ontario, Canada, 1969–78 ____ 120
Richard Frank, George J. Sirons, and Brian D. Ripley

Triazine herbicide residues in central European streams ____ 128
W. D. Hörmann, J. C. Tournayre, and H. Egli

APPENDIX ____ 132

Information for Contributors ____ 134

HUMANS

Sources of Parathion Exposures for Israeli Aerial Spray Workers, 1977

Bension Cohen,[1] Eliahu Richter,[2] Eliahu Weisenberg,[3] Judith Schoenberg,[3] and Menachem Luria [1,4]

ABSTRACT

Exposure of Israeli agricultural spray pilots and ground crews to parathion was studied. Measurements were made with personal samplers containing wet midget impingers; samples were analyzed by gas chromatography.

Cockpit air exposure levels during 11–21-minute sampling periods for 12 flights ranged from nearly 0 to 430 μg/m³. During sampling periods of 30 minutes to 4 hours the threshold limit value (TLV) of 100 μg/m³ was exceeded in 2 of 19 instances. In seven measurements of ground crew exposures, TLV was not exceeded. Air washing with parathion resulted in airborne contamination of the ground level area at more than three times the TLV. Skin exposure data suggested that this route of exposure was significant for ground crew workers but not for pilots. Calculations based on the present data and standard absorption formula suggested that total daily intake for ground crew, but not for pilots, exceeded the Accepted Daily Intake (ADI) of 5 μg/kg body weight. Sources of exposure and contamination for ground crew and pilots were identified. Recommended environmental control measures for parathion exposure should include cockpit air filtration, modification in flight patterns, paving landing areas, installation of hosing and drainage, NaOH neutralization point, and separate loading and unloading sites. Personal control measures were suggested as a supplement.

Introduction

The agricultural use of pesticides in Israel is very intensive relative to other countries. Among the most commonly used pesticides is parathion, mainly applied in 400 km² of cotton fields (*1*). During the last five years, parathion consumption has increased from 216 tons in 1973 to 830 tons in 1977 (*1*), all of which is applied during two to three summer months. The increased use of parathion for agricultural applications is related to its low cost and high efficiency against crop pests.

Highly toxic, parathion causes cholinesterase (ChE) inhibition in humans at low exposure levels. The threshold limit value (TLV) for parathion exposures is 100 μg/m³ over 8 hours or 300 μg/m³ for short-term limit exposures (STL) (*12*) provided no dermal absorption occurs. Besides the well known acute effects, repeated low exposures may cause slower nerve conductivity and abnormalities in muscle action potential (*8*), possibly at levels below those affecting ChE.

Parathion exposures of pilot and ground workers have been studied in terms of ambient concentration, respiratory and skin exposures, the decrease of ChE concentration in blood, and, more recently, parathion metabolites in urine. Wolfe et al. (*4, 15*) measured respiratory and skin exposures of various spray workers to several pesticides. Their results showed that for pilots, respiratory parathion doses averaged 0.02 mg/hour and skin exposure averaged 13 mg/hour. Although only a fraction of the parathion to which the skin is exposed penetrates the body, Wolfe et al. concluded that skin exposure is potentially more dangerous.

Higher skin and respiratory exposures were found among flag carriers and plane loaders. Medical examinations of air and ground crews of an aerial spray company by Davies et al. (*3*) revealed that ChE blood levels in one third of the workers had decreased significantly. The ChE decreases were correlated with increased amounts of *p*-nitrophenol (PNP) in the urine. Ware and Morgan (*14*) measured parathion concentrations in air as well as skin exposure of cotton field workers at various intervals after aerial spray. Parathion concentrations were not high enough to affect the common ChE test. However, PNP was detected in urine, and parathion was found in the serum.

The present research was performed among workers of an aerial spray company which employs about 50 pilots, 60 loaders, and 100 mechanics. The company sprays about 50 percent of the pesticides in Israel. During peak season, the company's pilots experience

[1] Department of Human Environmental Sciences, School of Applied Science and Technology, The Hebrew University of Jerusalem, Israel.
[2] Department of Medical Ecology, Hadassah Medical School, The Hebrew University of Jerusalem, Israel.
[3] Ministry of Health, The Government of Israel.
[4] To whom all correspondence should be addressed.

a heavy work burden which starts at 4 A.M. and includes 4–5 hours of spraying flights, 15–25 takeoffs and landings, several hundred hairpin turns, and frequent passes under power lines. During the spraying flights, the pilots were exposed to high temperatures, high g forces, noise vibration and various pesticides. Medical examinations since 1973 have shown a gradual increase in the number of workers with some decrease in ChE blood level. In 1976, 40 percent of the pilots' tests showed decreases of $\geqq$ 10 percent. Decreases of $\geqq$ 30 percent were found in 40 percent of mechanics' and 30 percent of loaders' tests. In view of the pilots' working conditions and the ground crews' medical data and accident rates, authors wanted to estimate ambient levels of parathion in the environment of aerial spraying workers, in order to identify and evaluate the sources of exposure and to propose means for control.

Sampling and Analysis

LABORATORY STUDY OF SAMPLERS

The present research required a sampler for field applications which could efficiently collect parathion aerosols and vapors. Several methods have been used for pesticide sampling from air (*13*). Two methods were examined for appropriateness to the present study: wet midget impingers, which are most commonly used in pesticide monitoring (*2, 14*), and packed absorption columns. In both cases, ethylene glycol was the absorption liquid and a Cassella personal sampler was used for the controlled air drawing.

For safety reasons, authors substituted malathion for parathion in most of the laboratory studies. Malathion is an organophosphorus insecticide with chemical structure and physical properties similar to those of parathion, but with a toxicity lower by a facter of $\sim$ 100. Malathion vapors and aerosols were generated inside a double-walled 200 $\times$ 80 $\times$ 60-cm inhalation chamber. Large sized particles, $>$20 microns in diameter, and small sized particles, $<$2 microns in diameter, were generated separately by two different atomizers. Vapors were created by evaporating known amounts of malathion or parathion in a closed glass dish. Samples were taken at periods ranging from 30 minutes to 4 hours, after which the collectors were taken for extraction and analysis. The extraction was performed according to the guidelines of the U.S. Environmental Protection Agency (*11*). Following extraction, the collected malathion or parathion was dissolved in 1 ml of pure hexane.

Analysis was performed on a Packard Model 807 gas chromatograph with the following instrument parameters and operating conditions:

Detector:	flame photometric
Column:	6-ft long $\times$ ¼-inch OD glass, packed with 5 percent OV-210 on Chromosorb W (AW)
Temperature:	column 225°C
Carrier gas:	nitrogen flowing at 40 ml/minute
Sensitivity:	1 ng malathion 1.6 ng parathion

Before and after every series of measurements, a standard sample of parathion or malathion was injected.

Results of the laboratory survey of samplers are summarized in Table 1. The results indicate that the most efficient method was the wet midget impinger. Moreover, resistance to air flow limited the amount of wool which could be used in the glass wool experiments. Therefore, the impingers with a collection efficiency of 82 $\pm$ 10 percent were chosen for the field study.

FIELD STUDY

Personal samplers were placed on the instrument panels in the cockpits for the study of pilot exposures. Ground crew exposures were determined by placing similar samplers on the chest pockets of the workers. Work site exposures were monitored by sampling the air at a fixed location at 1.5 m aboveground. After exposure, the ethylene glycol from the impinger was introduced into a bottle containing 60 ml distilled water. The inlet

TABLE 1. *Laboratory survey of samples for the collection of parathion aerosols and vapors*

Collector	No. of Experiments	Pesticide	% Efficiency		
			$<$2-μ particles	$>$20-μ particles	Vapor
Glass bead column:					
50 mm long $\times$ 20 mm ID glass column filled with ethylene glycol-coated 3-mm-diameter glass beads.	1	malathion	75		
Efficiency was studied by using 2 collectors in series.	2	malathion		58–71	
Glass wool column:					
20 mm ID tube, containing 0.3 g ethylene glycol–coated glass wool.	3	malathion	70–92		
2–3 columns in series for the efficiency test.	2	malathion		78–93	
Wet midget impinger:	2	malathion	78–87		
Impinger contains 15 ml ethylene glycol; 2nd and 3rd traps contained ethylene glycol–coated glass wool.	1	malathion		82	
	2	malathion			93
Wet midget impinger:	1	parathion			98
2 in series for efficiency determination.	1	parathion			80

pipe was carefully flushed with 10 ml hexane which was then added to the extraction bottle. The bottle was vigorously shaken for 60 seconds and was stored in a cool place until analysis. The stability of parathion in hexane under similar conditions has been tested and no degradation has been detected. Skin exposure of pilot and ground crews was estimated by the attachment of Whatman filter paper No. 1 dipped in ethylene glycol. Parathion was extracted from the filter paper according to the method described above. Parathion contamination of pilots' and ground crews' hands was evaluated by having them wash their hands with hexane, and extracting the parathion as described above.

Samples were taken during August and September 1977 between 5 A.M. and 9 A.M. at ambient temperatures of 18–30°C and relative humidity of 60–80 percent. Pilots and ground crews were informed of all exposure data.

Results

Parathion measurements in cockpits were divided into two groups. In the first, 12 samples were taken during a single flight of parathion spraying which lasted 11–21 minutes. The data are shown in Table 2. Parathion concentrations ranged from 0 to 440 mg/m³. In seven samples the TLV was exceeded, and in one sample, parathion exceeded the STL. Results of the longer sampling periods are summarized in Table 3. In this category, sampling duration ranged from 35 to 260 minutes in which the TLV was exceeded in two of 18 cases; STL was exeeceded in one of the two. Sample 1 in Table 3 was taken during the application of azodrin and can be considered as a control.

Table 4 describes seven personal samplings of aircraft loaders. In Table 5, the data of nine samples taken at the aircraft loading area are presented. In both cases parathion concentrations were below TLV. Parathion concentrations measured at other work sites are summarized in Table 6. Subthreshold ambient concentrations of parathion were found in the pesticide storage hut in Ashkelon. Concentrations exceeding STL were found in the two samples taken at the aircraft washing area. At the neighboring sites, high concentrations of parathion were found when the wind came from the direction of the washing area.

TABLE 2. *Ambient parathion concentrations sampled during 11–21-minute periods in cockpits of Israeli agricultural spray planes*

Sample No.	Date	Starting Hour	Sampling Duration, Min.	Concentration of Parathion, μg/m³ ± 10%	Status of Air Shuttle Opening	Detection by Pilot's Sense of Smell	Aircraft Model
1	Aug. 24	05:25	11	430	open	Detected	Snow
2	Aug. 16	07:50	12	9	open	Not Determined	Snow
3	Aug. 16	05:30	13	12	open	Not Determined	Pawnee Brave
4	Aug. 28	07:00	14	270	open	Slightly Detected	Snow
5	Aug. 17	06:30	15	ND	open	ND	Snow
6	Aug. 17	07:00	17	ND	open	ND	Snow
7	Aug. 24	07:45	17	190	open	Slightly Detected	Snow
8	Aug. 23	07:25	18	250	open	Not Determined	Snow
9	Aug. 24	06:10	18	160	open	ND	Snow
10	Aug. 24	06:30	18	250	open	ND	Snow
11	Aug. 18	05:35	20	92	closed	ND	Snow
12	Aug. 18	05:10	21	130	closed	ND	Snow

NOTE: ND = not detected.

TABLE 3. *Ambient parathion concentrations sampled during 35–260-minute periods in cockpits of Israeli agricultural spray planes*

Sample No.	Date	Starting Hour	Sampling Duration, Min.	Concentration of Parathion, μg/m³ ± 10%	Status of Air Shuttle Opening	Detection by Pilot's Sense of Smell	Aircraft Model
1[1]	Aug. 16	06:00	35	ND	—	Not Determined	Pawnee Brave
2	Aug. 31	05:40	35	35	open	ND	Snow
3	Aug. 24	05:15	38	43	—	Not Determined	Snow
4	Aug. 30	05:45	39	85	open	ND	Snow
5	Aug. 23	06:15	43	ND	open	Not Determined	Snow
6	Aug. 23	07:45	43	120	—	Not Determined	Snow
7	Aug. 29	05:20	44	22	open	ND	Snow
8	Aug. 23	05:50	45	18	open	Not Determined	Snow
9	Aug. 23	05:50	45	14	open	Not Determined	Snow
10	Aug. 17	05:10	54	2	partly open	Slightly Detected	Pawnee Brave
11	Aug. 31	07:20	63	14	closed	ND	Helicopter
12	Sept. 9	07:00	71	410	closed	Detected	Turbo Snow
13	Aug. 18	05:20	78	12	closed	ND	Pawnee Brave
14	Sept. 1	06:15	97	8	open	Not Determined	Snow
15	Sept. 1	05:45	111	18	closed	Slightly Detected	Snow
16	Sept. 9	05:15	114	11	open	ND	Snow
17	Aug. 30	06:20	190	23	open	ND	Snow
18	Sept. 9	05:00	191	8	—	Not Determined	Snow
19	Aug. 25	05:15	260	6	—	Not Determined	Snow

NOTE: ND = not detected.
[1] Sample taken during application of azodrin and can be considered a control.

TABLE 4. *Exposures of aircraft loaders to parathion, Ashkelon and Bee'ry Airfields, Israel*

Sample No.	Date	Place	Starting Hour	Sampling Duration, Min.	Concentration, μG/M³ ± 10%
1	Sept. 9	Ashkelon	05:00	35	67
2	Sept. 6	Bee'ry	05:25	100	15
3	Sept. 9	Ashkelon	05:00	107	23
4	Sept. 2	Ashkelon	04:30	112	39
5	Sept. 2	Ashkelon	04:15	147	40
6	Sept. 8	Ashkelon	05:00	155	14
7	Sept. 8	Ashkelon	05:00	175	11

Discussion

PILOT EXPOSURE

Pilots are exposed to pesticides in ambient air during two stages of their work: at the loading site and in flight. Pilots spend 20–40 minutes/day at the loading site where they are exposed to pesticide-contaminated dust, mist, and vapors. In-flight exposure results from flying back into clouds of pesticide aerosols and vapors which remain dispersed after spraying.

If the breathing rate of spray pilots is similar to that of battle pilots, approximately 25 liters/minute (*10*), then there is complete absorption of inhaled parathion (*4, 9, 15*). The values for respiratory parathion intake for the samples of longer duration of Table 3 can be calculated and are shown on Table 7.

Apart from sample No. 12, calculated values in the present report are similar to the 0.02 μg/hour reported by Wolfe et al. (*4, 15*) for pilots' respiratory exposure and are far below the Accepted Daily Intake (ADI). In sample No. 12, however, which was taken in a Turbo Snow aircraft, ADI probably was exceeded within less than one hour. More samples would have been needed to determine whether to attribute this level to cockpit sealing defects or to temperature and wind conditions prevailing in the region.

For some of the short-term samples, wind speed and direction were also measured. These values were then examined in relation to two categories: wind directed 45–135° to spray line (type 1); and wind either parallel to spray line or nearly absent (type 2).

The present data show that high cockpit concentrations were measured only when type 2 wind conditions prevailed. Type 1 wind conditions were associated with low concentrations. The present findings confirm the influence of wind conditions on cockpit exposure level reported previously (*4, 15*). Also, they may explain the wide concentration range found mainly in the short-time samples. These concentrations may be the average of several instant peaks, which pilots smell (Tables 2, 3).

Pilots tend to leave the aeration shuttle open when releasing the spray load. In sample No. 12, Table 3, despite the ventilation shuttle always being kept closed,

TABLE 5. *Air sampling for parathion at aircraft loading areas, Ashkelon and Plugot Airfields, Israel*

Sample No.	Date	Place	Starting Hour	Sampling Duration, Min.	Concentration of Parathion, μG/M³ ± 10%	Sampling Method
1	Aug. 16	Ashkelon	05:45	150	6	impinger
2	Aug. 25	Ashkelon	04:50	154	20	impinger
3	Aug. 25	Ashkelon	05:00	106	13	cyclone
4	Aug. 29	Plugot	05:30	218	36	impinger
5	Aug. 29	Ashkelon	05:45	32	15	impinger
6	Sept. 1	Ashkelon	05:45	200	4	impinger
7	Sept. 1	Ashkelon	06:40	91	4	impinger
8	Sept. 11	Ashkelon	04:35	60	60	impinger
9	Sept. 11	Ashkelon	06:00	60	63	cyclone

TABLE 6. *Ambient concentrations of parathion at various worksites, Ashkelon and Herzelia Airfields, Israel*

Sample No.	Location	Date	Site	Starting Hour	Sampling Duration, Min.	Concentration of Parathion, μG/M³ ± 10%	Remarks
1	Ashkelon	Sept. 7	Pesticide storage hut	07:00	170	1	
2	Ashkelon	Aug. 17		03:20	287	2	
3	Ashkelon	Aug. 24		04:10	218	25	Extremely hot day (>35°C) puddles of water and pesticides on the floor
4	Ashkelon	Aug. 25		04:10	230	2	Cooler day, clean floor
5	Ashkelon	Aug. 17	Office	07:00	221	3	
6	Herzelia	Sept. 20	Mechanical workshop	12:00	100	19	
7	Herzelia	Sept. 21	Aircraft washing area	11:00	85	290	Wind blows from washing area towards garage and offices
8	Herzelia	Sept. 23		11:00	108	350	
9	Herzelia	Sept. 23	Offices front	11:00	97	43	
10	Herzelia	Sept. 23	Aircraft garage	11:00	110	97	
11	Herzelia	Sept. 26		11:00	107	12	Wind blows in opposite direction from garage and offices.

TABLE 7. *Respiratory intakes of parathion by pilots of Israeli agriculture spray service*

Sample No. From Table 3	Duration, Min.	Ambient Parathion Concentration, μG/M³	Total Parathion Inhaled, μG	μG Parathion Inhaled/Hour
12	71	410	730	620
13	78	12	23	18
14	79	8	16	12
15	111	18	50	27
16	144	11	40	17
17	190	23	110	35
18	191	8	38	12
19	260	6	36	9

the pilot smelled parathion during the flight. This case suggested the possibility of routes of penetration into the cockpit other than via the shuttle. Authors did not observe an association between parathion concentration and aircraft type.

Two possible explanations offered for the lower parathion concentration measured with the longer sampling periods are time dilution of the instant peak, and the spraying of pesticides other than parathion during sampling.

GROUND CREW EXPOSURE

Visual observation indicated that crews are exposed to parathion and other pesticides by contaminated dust blown and dispersed from the unpaved ground when the aircraft takes off and from vapor from puddles and contaminated equipment.

The respiratory parathion intake can be calculated from the results of the ground crew personal sampling (Table 4). If the ventilation rate is 25 liters/minute, and there is complete absorption of inhaled parathion, then respiratory intake alone is in the range of 46–176 μg; ADI is ~ 400 μg. Parathion concentration measured in the ambient air at the fixed loading area sites (Table 5) were in the range of concentration measured with personal samplers attached to workers' pockets.

Several ground crew workers became nauseated when smelling the pesticides and experienced headaches and malaise while working at the pesticide storage hut near Ashkelon. Measurement at the site (Table 6) suggested that ambient parathion concentration remained low when the hut was kept clean. However, a combination of hot days and puddles containing pesticides on the hut floor might result in tenfold higher concentration (Table 6). The 25 μg/m³ level found, although still below TLV, is probably one ingredient in a cocktail of vapors of pesticides stored in the poorly ventilated hut.

Herzelia airport serves as the company's central airport where its offices and maintenance and repair shop are located. During summers, episodes of acute poisoning were reported among administrative personnel. As shown in Table 6, aircraft washers seem to have the closest contact with pesticides. They experience parathion concentrations which apparently exceeded STL for several hours a day. They are exposed mainly to aerosols including those produced during washing or when the aircraft is taxiing. Ground crew use of protective equipment, such as boots, rubber aprons, gloves, and masks probably prevents more frequent, and more serious episodes. Authors feel that the washing area, which is at the center of the airport complex, is a major source of exposure for workers in the workshop, offices, and garage, which are all within 20–40 m of it. The sample taken at the entrance of the neighboring workshop hut was collected 1–2 hours after plane washing. This value may be considered as the background parathion concentration.

SKIN EXPOSURE

Despite the well known difficulties associated with measuring skin exposure and estimating the absorption, most authorities are convinced that skin exposure exceeds respiratory exposure. Total dermal absorption is a function of exposed skin area, anatomic region (*7*), and ambient temperature (*6*). Pilots and ground crews usually wear freshly cleaned long-sleeved overalls. This reduces average exposed skin area to approximately 2000 cm² (*5*). At the same time, high temperature, sweating, exposure lasting several hours, and delays before showering all seem to enhance skin penetration.

Eight studies showed that pilots are exposed to 5–200 μg/hour dermally; ground crews' skin exposure is 40–5000 μg/hour. Calculations based on an absorption ratio of 10 percent (*7*) suggest that total absorption for pilots is up to 20 μg/hour and for ground crews as much as 500 μg/hour. For pilots, dermal absorption seemed to be in the same range as respiratory exposure. However, for ground crews, parathion absorption via skin exposure alone could exceed the ADI.

Direct hand contact provided a further opportunity for parathion penetration. In six hexane hand wash measurements, it was shown that as much as 4000 μg can be washed off. Opportunities for ground crew hand contact exposure included preparing and loading the pesticide, holding loading pipes, and cleaning cockpit windshields. Gloves were seldom used.

Our flight exposure data (Tables 2, 3) specifically indicated that sense of smell could not be relied upon in all instances to detect possibly hazardous parathion air exposures.

Conclusion

Recommended environmental control measures for parathion exposure included paving of the landing area, drainage, NaOH neutralization points, separate loading and unloading sites, and hosing arrangements. Recommended personal control measures included wearing impermeable uniforms, boots, and gloves, and proper mask use, storage, and maintenance.

Control of airborne exposure to the pilot in the cockpit via both inhalation and skin absorption would require absolute filters to prevent aerosol penetration to the cockpit along with air ventilation and cooling to decrease pilot discomfort. In addition, modification of flight patterns, in certain settings, might reduce aircraft exposure to the sprayed aerosol plume.

Personal air and skin sampling is helpful in assessing and tracing sources of air and skin exposure and contamination by parathion in the context of a comprehensive surveillance and control program for agricultural spray pilots and ground crews.

LITERATURE CITED

(1) *Cotton Production and Marketing Board, Ltd. 1976.* Management report and private information. Tel Aviv, Israel.

(2) *Culver, D., P. Caplan, and G. S. Batchelor. 1956.* Studies of human exposure during aerosol application of malathion and chlorthion. AMA Arch. Ind. Health 13(1):37–50.

(3) *Davies, J. E., M. T. Shafik, A. Barquet, C. Morgade, and J. X. Danauskas. 1976.* Worker reentry safety: a medical overview of reentry periods and the use of urinary alkylphosphates in human pesticide monitoring. Residue Rev. 62:45–47.

(4) *Durham, W. F., and H. R. Wolfe. 1963.* An additional note regarding measurements of the exposure of workers to pesticides. Bull. World Health Org. 29(2):279–281.

(5) *Gunther, F. A., Y. Iwata, G. E. Carman, and C. A. Smith. 1977.* The citrus reentry problem: research on its cause and effects and approaches to its minimization. Residue Rev. 67:1–132.

(6) *Hayes, G. R., A. J. Funchas, and W. V. Hartwell. 1964.* Dermal exposure of human volunteers to parathion. Arch. Environ. Health 8:829–833.

(7) *Maibach, H. I., R. J. Feldman, T. H. Milby, and W. F. Serat. 1971.* Regional variation in percutaneous penetration in man. Arch. Environ. Health 23(9): 208–211.

(8) *Roberts, D. V. 1976.* EMG voltage and motor nerve conduction velocity in OP pesticide factory workers. Int. Arch. Occup. Environ. Health 36(4):267–274.

(9) *Simpson, G. R., and A. Beck. 1965.* Exposure to parathion: dermal and inhalation exposure to parathion while spraying tomato bushes with a knapsack mister. Arch. Environ. Health 11(12):784–786.

(10) *U.S. Air Force. 1953.* Medical Service: physiology of flight. AFP 160–10(4):16.

(11) *U.S. Environmental Protection Agency. 1977.* Manual of analytical methods for the analysis of pesticide residues in human and environmental samples. Section 8/A.

(12) *U.S. National Institute for Occupational Safety and Health.* Criteria for a recommended standard of occupational exposure to parathion.

(13) *Van Dyk, L. P., and K. Visweswariah. 1975.* Pesticides in air: sampling methods. Residue Rev. 55:91–134.

(14) *Ware, G. W., and D. P. Morgan. 1976.* Worker reentry safety: Techniques of determining safe reentry intervals for organophosphate-treated cotton fields. Residue Rev. 62:79–100.

(15) *Wolfe, H. R., W. F. Durham, and J. F. Armstrong. 1967.* Exposure of workers to pesticides. Arch. Environ. Health 14(4):622–633.

FOOD AND FEED

Pesticides and Other Chemical Residues in Infant and Toddler Total Diet Samples—(I)—August 1974–July 1975 [1]

Roger D. Johnson, Dennis D. Manske, Dallas H. New, and David S. Podrebarac

ABSTRACT

Since 1964, the Food and Drug Administration, U.S. Department of Health, Education and Welfare, has reported residues of pesticides and other chemicals present in the average diet of the young adult male. The present report is the first in a series of market baskets whose purpose is to monitor the average diet of infants and toddlers for the same residues. Ten market baskets were collected in 10 cities which ranged in population from less than 50,000 to 1,000,000 or more. Averages and ranges of residues found are reported by food class. Results of recovery studies of known residues and chemicals within various food classes are also presented.

Introduction

Since 1964, the Food and Drug Administration (FDA), U.S. Department of Health, Education and Welfare, reported residues of pesticides and other chemicals ingested in the average diet of the United States' largest eater, the young adult male (*1, 10*). Although changes have been made in sampling frequency, areas sampled, analytical methods, and types of residues sought, the program has continued essentially in the same form until the present. During this, the eleventh year of the study, the program has been broadened in scope by replacing 10 of the original 30 adult market baskets with 10 infant and toddler market baskets representing a basic 14-day diet for infants and for toddlers. The FDA's Office of Nutrition and Consumer Services, Bureau of Foods, has used available 1965 U.S. Department of Agriculture survey data to calculate the average daily consumption of particular foods and food groups for 6-month-old infants and 2-year-old toddlers from four geographic regions of the United States, i.e., South, Northeast, North Central, and West.

The foods were prepared by a dietitian in the manner in which a consumer would prepare and serve them at home. Food items were separated into 11 commodity classes as listed in Table 1. Each class was then composited into a slurry and analyzed for organochlorine and organophosphorus pesticides, carbaryl, herbicides, metals including selenium, zinc, cadmium, mercury, lead, and arsenic; and industrial chemicals including polychlorinated biphenyls (PCBs) and pentachlorobenzene. Methodology included atomic absorption spec-

TABLE 1. *Commodity classes of infant and toddler foods analyzed for pesticides and other chemical residues, August 1974—July 1975*

KEY	FOOD CLASS
I	Drinking water[1]
II	Whole milk, fresh[1]
III	Other dairy and substitutions, infant
	Other dairy and substitutions, toddler
IV	Meat, fish, and poultry, infant
	Meat, fish, and poultry, toddler
V	Grain and cereal products, infant
	Grain and cereal products, toddler
VI	Potatoes[1,2]
VII	Vegetables, infant
	Vegetables, toddler
VIII	Fruit and fruit juice, infant
	Fruit and fruit juice, toddler
IX	Oils and fats[1,3]
X	Sugar and adjuncts, infant
	Sugar and adjuncts, toddler
XI	Beverages[1,4]

NOTE: Use key with Table 3.

[1] Due to similarity in diet between infants and toddlers for certain classes of foods, single determinations are made and reported for both.

[2] No infant composite for western region.

[3] No infant composite for the north central, western, and southern regions.

[4] No infant composite from north central region.

[1] Kansas City District Office Laboratory, Food and Drug Administration, U.S. Department of Health, Education and Welfare, Kansas City, Mo. 64106.

troscopy, fluorometry, gas chromatography, thin-layer chromatography, mass spectroscopy, and established extraction and cleanup techniques (*2–9, 11*). Conditions, techniques, and limits of quantitation were described in the adult market baskets series, with the exception of the water composite.

The water composite was extracted with methylene chloride, and the extracts were dried by passage through sodium sulfate and were evaporated to a small volume (*12*). The equivalent of 1000 mg water was injected into a gas chromatograph. The limit of detection was set at 0.0002 ppm heptachlor epoxide.

Results

In the infant market basket, authors found 306 residues of 28 different compounds; 121 residues were at the trace level. In the toddler market basket, authors found 468 residues of 30 different compounds; 179 were at the trace level. The 32 different residues found are listed in decreasing order of frequency in Table 2. Methoxychlor and parathion were found only in infant food composites; ronnel, endosulfan, TCNB, and leptophos were found only in toddler food composites. Table 3 shows the frequency of occurrences of residues by food class, and Table 4 shows the levels of chemical residues found within each food class. The average stated in Table 4 is based on the total number of composites examined for that food class. No trace residues have been included in calculating the average.

The most common residues and their maximum levels are discussed below for each of the 11 food classes. No findings have been corrected for recoveries.

DRINKING WATER

Tap water composites were collected from the same areas as the market baskets, and single determinations were made and reported for both infant and toddler classes. The tap water was used throughout the market basket study in the preparation of other items requiring dilution or addition of water. Six of the 10 water samples contained zinc, ranging from 0.1 ppm to 0.7 ppm and averaging 0.2 ppm. Cadmium was also found in one of the market baskets at the trace level.

WHOLE MILK, FRESH

This composite was common to both infant and toddler classes. Zinc was reported most frequently, in all 10 market baskets, ranging from 2.5 ppm to 5.2 ppm and averaging 3.7 ppm. Dieldrin was found in four market baskets, ranging from 0.001 ppm to 0.002 ppm and averaging a trace for all baskets. Half the market baskets showed DDE residues in the range 0.001–0.005 ppm with an average of 0.001 ppm. Other reportable residues included benzene hexachloride (BHC), heptachlor epoxide, selenium, and HCB.

TABLE 2. *Chemical residues found in infant and toddler food composites from 10 United States cities—August 1974–July 1975*

Chemical Found	No. of Composites With Residues	No. of Positive Composites With Residues Reported as Trace [1]	Range, ppm
INFANT			
Zinc	92	0	0.10–41.8
Cadmium	41	35	0.05–0.10
Selenium	32	15	0.10–0.30
Lead	28	17	0.10–0.31
Dieldrin	20	9	0.001–0.006
DDE	15	3	0.001–0.024
Mercury	1	1	T
BHC	14	9	T–0.002
Malathion	13	1	0.006–0.173
Diazinon	7	7	T
HCB	7	4	0.001–0.004
Heptachlor epoxide	6	4	0.001
Lindane	3	1	0.008–0.012
Toxaphene	3	0	0.16–0.51
Botran	3	0	0.001–0.013
p,p'-TDE	2	2	T
Carbaryl	2	2	T
PCNB	2	1	0.03
PCA	2	0	0.003–0.008
Arsenic	5	5	T
DDT	1	1	T
Methoxychlor	1	1	T
Parathion	1	1	T
CIPC	1	0	0.051
PCB	1	1	T
PCP	1	0	0.01
Octachlor epoxide	1	1	T
Pentachlorobenzene	1	0	0.002
TODDLER			
Zinc	105	0	0.10–41.4
Cadmium	61	50	0.05–0.08
Selenium	44	24	0.14–0.34
Dieldrin	34	8	0.001–0.007
Lead	31	18	0.10–0.22
BHC	31	14	T–0.003
DDE	24	4	0.001–0.064
Lindane	20	8	0.001–0.007
Malathion	18	1	0.004–0.125
Heptachlor epoxide	17	14	0.001–0.002
Diazinon	12	7	0.001–0.003
HCB	12	7	0.001–0.008
Arsenic	9	4	0.100–0.180
Mercury	8	7	0.02
TDE	6	5	0.004
CIPC	6	0	0.011–0.120
Botran	6	0	0.001–0.024
DDT	5	4	0.007
PCA	5	1	0.003–0.030
Toxaphene	4	1	0.100–0.260
PCNB	4	1	0.004–0.016
Pentachlorobenzene	4	2	0.006
Carbaryl	2	1	0.010
Aroclor 1254	2	2	T
Ronnel	1	1	T
Endosulfan	1	0	0.006
TCNB	1	1	T
PCP	1	0	0.090
Octachlor epoxide	1	1	T
Phosvel	1	0	0.005

[1] Chemicals capable of being detected by the specific analytical methodology may be confirmed quantitatively but are not quantifiable when they are present at concentrations below the limit of quantitation. Limit of quantitation varies with residues and food classes.

OTHER DAIRY AND SUBSTITUTIONS

Infant.—Variations in infants' and toddlers' diet are evident in this composite. The infant food composite

TABLE 3. *Frequency of occurrence of chemical residues, by food class, in infant and toddler food composites from 10 United States cities—August 1974–July 1975*

Chemical	Food Class[1]										
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
NUMBER OF OCCURRENCES IN INFANT FOODS											
Zinc	6	10	10	10	10	7	10	10	3	8	8
Cadmium	1	—	1	6	10	7	10	1	3	1	1
Selenium	—	3	3	10	10	—	2	—	2	2	—
Lead	—	—	2	4	5	1	6	6	—	1	3
Dieldrin	—	4	4	7	1	2	—	—	2	—	—
DDE	—	5	4	4	—	—	2	—	—	—	—
Arsenic	—	—	—	1	—	—	1	2	—	1	—
BHC	—	6	5	3	—	—	—	—	—	—	—
Malathion	—	—	—	—	10	—	—	—	3	—	—
Diazinon	—	—	—	—	4	1	1	—	—	1	—
HCB	—	2	1	3	—	—	—	—	1	—	—
Heptachlor epoxide	—	2	1	3	—	—	—	—	—	—	—
Lindane	—	—	—	—	2	1	—	—	—	—	—
Toxaphene	—	—	—	—	—	—	—	—	3	—	—
Botran®	—	—	—	—	—	—	—	3	—	—	—
p,p'-TDE	—	—	—	1	—	—	1	—	—	—	—
Carbaryl	—	—	—	—	—	—	—	1	—	1	—
PCNB	—	—	—	—	—	—	—	—	2	—	—
PCA	—	—	—	—	—	—	1	—	1	—	—
Mercury	—	—	—	1	—	—	—	—	—	—	—
p,p'-DDT	—	—	—	1	—	—	—	—	—	—	—
Methoxychlor	—	—	1	—	—	—	—	—	—	—	—
Parathion	—	—	—	—	—	—	1	—	—	—	—
CIPC	—	—	—	—	—	1	—	—	—	—	—
PCP	—	—	—	—	—	—	1	—	—	—	—
PCB	—	—	—	1	—	—	—	—	—	—	—
Octachlor epoxide	—	—	—	1	—	—	—	—	—	—	—
Pentachlorobenzene	—	—	—	—	—	—	—	—	1	—	—
NUMBER OF OCCURRENCES IN TODDLER FOODS											
Zinc	6	10	10	10	10	10	10	10	10	10	9
Cadmium	1	—	3	5	10	10	10	2	10	8	2
Dieldrin	—	4	9	10	1	4	2	—	4	—	—
Selenium	—	3	5	10	10	1	1	—	8	6	—
Lead	—	—	1	3	4	3	10	4	—	3	3
BHC	—	6	10	7	—	—	3	—	—	5	—
DDE	—	5	8	9	—	—	1	—	—	1	—
Lindane	—	—	1	2	—	1	7	—	—	9	—
Malathion	—	—	—	—	9	—	—	—	6	3	—
Heptachlor epoxide	—	2	8	7	—	—	—	—	—	—	—
Diazinon	—	—	1	1	5	1	1	1	—	2	—
HCB	—	2	3	3	—	—	—	—	4	—	—
Arsenic	—	—	1	5	—	—	—	2	—	1	—
TDE	—	—	1	4	—	—	—	—	—	1	—
CIPC	—	—	—	—	—	5	—	1	—	—	—
Botran®	—	—	—	—	—	—	—	4	—	2	—
DDT	—	—	1	4	—	—	—	—	—	—	—
PCA	—	—	—	—	—	—	—	—	5	—	—
Toxaphene	—	—	—	—	—	—	—	—	4	—	—
PCNB	—	—	—	—	—	—	—	—	4	—	—
Pentachlorobenzene	—	—	—	—	—	—	—	—	4	—	—
Carbaryl	—	—	—	—	—	—	1	1	—	—	—
Ronnel	—	—	1	—	—	—	—	—	—	—	—
Endosulfan	—	—	—	—	—	—	—	1	—	—	—
TCNB	—	—	—	—	1	—	—	—	—	—	—
PCP	—	—	—	—	—	—	—	—	—	1	—
Octachlor epoxide	—	—	—	1	—	—	—	—	—	—	—
Phosvel	—	—	—	—	—	—	1	—	—	—	—
Mercury	—	—	—	8	—	—	—	—	—	—	—
Aroclor 1254	—	—	—	1	—	—	—	—	1	—	—
Endosulfan sulfate	—	—	—	—	—	—	—	1	—	—	—

[1] See Table 1 for key to food classes.

included evaporated milk and various formula preparations. Zinc was found in all 10 market baskets, ranging from 0.9 ppm to 6.5 ppm, and averaging 4.5 ppm. BHC averaged a trace in five market baskets; range was 0.001–0.002 ppm. Three of the 10 baskets contained trace to 0.12 ppm selenium; average was 0.01 ppm selenium. Residues of heptachlor epoxide, HCB, methoxychlor, lead, and cadmium were also found.

Toddler.—The toddlers' food composite included ice cream, chocolate milk, skim milk, cheese, and lesser amounts of other products such as half and half, fudgesicles, and puddings. Zinc and BHC were found in all 10 baskets at 2.2–7.8 ppm (average 5.6 ppm) and 0.001–0.003 ppm (average 0.002 ppm), respectively. Dieldrin was reported for nine market baskets, ranging from 0.002 ppm to 0.007 ppm and averaging 0.004 ppm; DDE and heptachlor epoxide were found in eight market baskets at 0.003 to 0.012 ppm, average 0.004 ppm) and trace to 0.002 ppm (average trace), respectively. Selenium was found in five market baskets at the trace level. Authors also found residues of HCB, cadmium, lindane, diazinon, ronnel, arsenic, DDT, TDE, and lead.

MEAT, FISH, AND POULTRY

Infant.—This composite contained the greatest number of residues, eight organochlorines, six metals, and one industrial chemical. Some regions limited the infant diet to commercially prepared meat-vegetable products, whereas others included fresh meat and eggs. Food composites from all 10 market baskets contained selenium, ranging from 0.10 ppm to 0.19 ppm and averaging 0.08 ppm, and zinc, ranging from 8.2 ppm to 41.8 ppm and averaging 19.1 ppm. Dieldrin levels of 0.001–0.003 ppm, average 0.001 ppm, were found in seven market baskets. DDE residues were found in four of the 10 market baskets, ranging from 0.005 ppm to 0.024 ppm and averaging 0.004 ppm. Other pesticide and metal residues reported near the trace level included BHC, heptachlor epoxide, HCB, DDT, TDE, octachlor epoxide, mercury, arsenic, lead, and cadmium. PCBs were found at trace level in the composite of one market basket.

Toddler.—Food composites in this category likewise contained the greatest number of residues: nine organochlorines, six metals, one organophosphate, and one industrial chemical. Fresh meats, fish, and poultry products, similar to the adult market basket, were composited. Three residues were found in all 10 market baskets: dieldrin, 0.002–0.004 ppm, average 0.002 ppm; selenium, 0.15–0.34 ppm, average 0.23 ppm; and zinc, 23.2–41.4 ppm, average 31.7 ppm. DDE was reported for nine market baskets ranging from 0.002 ppm to 0.064 ppm and averaging 0.012 ppm. Mercury was reported in eight market baskets at trace to 0.02 ppm levels, and averaging trace. Arsenic residues averaged 0.06 ppm in five market baskets; range was 0.10–0.18 ppm. Lead was found in three meat composites of the 10 analyzed, with results of 0.10 ppm, 0.11 ppm, and trace, averaging 0.02 ppm. Other reportable residues included BHC, cadmium, heptachlor epoxide, lindane, DDT, TDE, HCB, diazinon, octachlor epoxide, and PCBs.

GRAIN AND CEREAL PRODUCTS

Infant.—The predominant ingredients in the composites were dry cereals and flour, corn, or bread. Residues

TABLE 4. *Levels of chemical residues, by food class, of infant and toddler food composites from 10 United States cities—August 1974–July 1975*

Chemical	Residue, ppm		Chemical	Residue, ppm	
	Infant	Toddler		Infant	Toddler
I. DRINKING WATER					
ZINC			CADMIUM		
Average	0.2	0.2	Average	T	T
Positive composites			Positive Composites		
Total number	6	6	Total number	1	1
Number reported as trace	0	0	Number reported as trace	1	1
Range	0.1–0.7	0.1–0.7	Range	T	T
II. WHOLE MILK, FRESH					
ZINC			BHC		
Average	3.7	3.7	Average	0.0002	0.0002
Positive composites			Positive composites		
Total number	10	10	Total number	6	0
Number reported as trace	0	0	Number reported as trace	3	3
Range	2.5–5.2	2.5–5.2	Range	0.0004–0.001	0.0004–0.0010
DIELDRIN			HEPTACHLOR EPOXIDE		
Average	T	T	Average	T	T
Positive composites			Positive composites		
Total number	4	4	Total number	2	2
Number reported as trace	2	2	Number reported as trace	1	1
Range	0.001–0.002	0.001–0.002	Range	T–0.001	T–0.001
DDE			SELENIUM		
Average	0.001	0.001	Average	T	T
Positive composites			Positive composites		
Total number	5	5	Total number	3	3
Number reported as trace	1	1	Number reported as trace	3	3
Range	0.001–0.005	0.001–0.005	Range	T	T
HCB					
Average	T	T			
Positive composites					
Total number	2	2			
Number reported as trace	2	2			
Range	T	T			
III. OTHER DAIRY AND SUBSTITUTIONS					
ZINC			LINDANE		
Average	4.5	5.6	Average		T
Positive composites			Positive composites		
Total number	10	10	Total number		1
Number reported as trace	0	0	Number reported as trace		1
Range	0.9–6.5	2.20–7.80	Range		T
DIELDRIN			ARSENIC		
Average	T	0.004	Average		T
Positive composites			Positive composites		
Total number	4	9	Total number		1
Number reported as trace	3	0	Number reported as trace		1
Range	T–0.002	0.002–0.007	Range		T
DDE			BHC		
Average	T	0.004	Average	T	0.002
Positive composites			Positive composites		
Total number	4	8	Total number	5	10
Number reported as trace	2	2	Number reported as trace	3	2
Range	0.002–0.003	0.003–0.012	Range	0.001–0.002	0.001–0.003
TDE			HEPTACHLOR EPOXIDE		
Average		T	Average	T	T
Positive composites			Positive composites		
Total number		1	Total number	1	8
Number reported as trace		1	Number reported as trace	0	6
Range		T	Range	0.001	T–0.002
SELENIUM			DDT		
Average	0.01	T	Average		T
Positive composites			Positive composites		
Total number	3	5	Total number		1
Number reported as trace	2	5	Number reported as trace		1
Range	T–0.12	T	Range		T
CADMIUM			LEAD		
Average	T	0.01	Average	T	T
Positive composites			Positive composites		
Total number	1	3	Total number	2	1
Number reported as trace	1	2	Number reported as trace	2	1
Range	T	T–0.07	Range	T	T

(Continued next page)

TABLE 4. (Cont'd). *Levels of residues, by food class, of infant and toddler food composites from 10 United States cities—August 1974–July 1975*

Chemical	Residue, ppm		Chemical	Residue, ppm	
	Infant	Toddler		Infant	Toddler
III. OTHER DAIRY AND SUBSTITUTIONS *(Cont'd)*					
RONNEL			**HCB**		
Average		T	Average	T	T
Positive composites			Positive composites		
Total number		1	Total number	1	3
Number reported as trace		1	Number reported as trace	1	2
Range		T	Range	T	T–0.001
DIAZINON			**METHOXYCHLOR**		
Average		T	Average	T	
Positive composites			Positive composites		
Total number		1	Total number	1	
Number reported as trace		0	Number reported as trace	1	
Range		0.002	Range	T	
IV. MEAT, FISH, AND POULTRY					
ZINC			**DDT**		
Average	19.1	31.7	Average	T	0.001
Positive composites			Positive composites		
Total number	10	10	Total number	1	4
Number reported as trace	0	0	Number reported as trace	1	3
Range	8.2–41.8	23.2–41.4	Range	T	T–0.007
MERCURY			**TDE**		
Average	T	T	Average	T	T
Positive composites			Positive composites		
Total number	1	8	Total number	1	4
Number reported as trace	1	7	Number reported as trace	1	3
Range	T	T–0.02	Range	T	T–0.004
ARSENIC			**LEAD**		
Average	T	0.06	Average	0.01	0.02
Positive composites			Positive composites		
Total number	1	5	Total number	4	3
Number reported as trace	1	1	Number reported as trace	3	1
Range	T	0.10–0.18	Range	T–0.10	0.10–0.11
BHC			**PCB**		
Average	T	T	Average	T	T
Positive composites			Positive composites		
Total number	3	7	Total number	1	1
Number reported as trace	3	5	Number reported as trace	1	1
Range	T	T–0.001	Range	T	T
LINDANE			**OCTACHLOR EPOXIDE**		
Average		T	Average	T	T
Positive composites			Positive composites		
Total number		2	Total number	1	1
Number reported as trace		2	Number reported as trace	1	1
Range		T	Range	T	T
SELENIUM			**DDE**		
Average	0.8	0.23	Average	0.004	0.012
Positive composites			Positive composites		
Total number	10	10	Total number	4	9
Number reported as trace	4	0	Number reported as trace	0	0
Range	0.10–0.19	0.15–0.34	Range	0.005–0.024	0.002–0.064
CADMIUM			**HCB**		
Average	T	T	Average	T	T
Positive composites			Positive composites		
Total number	6	5	Total number	3	3
Number reported as trace	6	5	Number reported as trace	1	1
Range	T	T	Range	0.001–0.004	T–0.003
DIELDRIN			**DIAZINON**		
Average	0.001	0.002	Average		T
Positive composites			Positive composites		
Total number	7	10	Total number		1
Number reported as trace	2	1	Number reported as trace		1
Range	0.001–0.003	0.002–0.004	Range		T
HEPTACHLOR EPOXIDE					
Average	T	T			
Positive composites					
Total number	3	7			
Number reported as trace	3	7			
Range	T	T			

(Continued next page)

TABLE 4. (Cont'd). *Levels of residues, by food class, of infant and toddler food composites from 10 United States cities—August 1974–July 1975*

Chemical	Residue, ppm		Chemical	Residue, ppm	
	Infant	Toddler		Infant	Toddler
V. GRAIN AND CEREAL PRODUCTS					
ZINC			SELENIUM		
Average	13.9	8.0	Average	0.23	0.22
Positive composites			Positive composites		
Total number	10	10	Total number	10	10
Number reported as trace	0	0	Number reported as trace	0	0
Range	9.1–18.4	5.4–9.9	Range	0.20–0.30	0.14–0.30
LEAD			CADMIUM		
Average	0.073	0.03	Average	T	T
Positive composites			Positive composites		
Total number	5	4	Total number	10	10
Number reported as trace	2	2	Number reported as trace	10	10
Range	0.20–0.31	0.10–0.16	Range	T	T
MALATHION			DIAZINON		
Average	0.017	0.009	Average	T	T
Positive composites			Positive composites		
Total number	10	9	Total number	4	5
Number reported as trace	1	0	Number reported as trace	4	3
Range	0.006–0.039	0.004–0.018	Range	T	0.002–0.003
TCNB			LINDANE		
Average		T	Average	0.002	
Positive composites			Positive composites		
Total number		1	Total number	2	
Number reported as trace		1	Number reported as trace	0	
Range		T	Range	0.008–0.012	
			DIELDRIN		
			Average	T	T
			Positive composites		
			Total number	1	1
			Number reported as trace	1	0
			Range	T	0.003
VI. POTATOES					
ZINC			CADMIUM		
Average	3.8	3.7	Average	0.01	0.03
Positive composites			Positive composites		
Total number	7	10	Total number	7	10
Number reported as trace	0	0	Number reported as trace	5	4
Range	2.1–6.8	2.5–6.8	Range	T–0.05	0.05–0.06
DIELDRIN			LINDANE		
Average	0.001	0.001	Average	T	T
Positive composites			Positive composites		
Total number	2	4	Total number	1	1
Number reported as trace	0	1	Number reported as trace	1	1
Range	0.004–0.005	0.002–0.005	Range	T	T
CIPC			LEAD		
Average	0.007	0.015	Average	T	T
Positive composites			Positive composites		
Total number	1	5	Total number	1	3
Number reported as trace	0	0	Number reported as trace	1	3
Range	0.051	0.011–0.052	Range	T	T
DIAZINON			SELENIUM		
Average	T	T	Average		T
Positive composites			Positive composites		
Total number	1	1	Total number		1
Number reported as trace	1	1	Number reported as trace		1
Range	T	T	Range		T
VII. VEGETABLES					
ZINC			CARBARYL		
Average	4.6	4.4	Average		T
Positive composites			Positive composites		
Total number	10	10	Total number		1
Number reported as trace	0	0	Number reported as trace		0
Range	3.0–7.9	3.4–6.4	Range		0.01
CADMIUM			DIAZINON		
Average	0.01	T	Average	T	T
Positive composites			Positive composites		
Total number	10	10	Total number	1	1
Number reported as trace	9	10	Number reported as trace	1	0
Range	T–0.08	T	Range	T	0.001

(Continued next page)

TABLE 4. (Cont'd). *Levels of residues, by food class, of infant and toddler food composites from 10 United States cities—August 1974–July 1975*

Chemical	Residue, ppm		Chemical	Residue, ppm	
	Infant	Toddler		Infant	Toddler
VII. VEGETABLES *(Cont'd)*					
DDE			**BHC**		
Average	0.001	T	Average		T
Positive composites			Positive composites		
Total number	2	1	Total number		3
Number reported as trace	0	0	Number reported as trace		0
Range	0.002–0.011	0.002	Range		0.001–0.002
SELENIUM			**DIELDRIN**		
Average	T	T	Average		T
Positive composites			Positive composites		
Total number	2	1	Total number		2
Number reported as trace	2	1	Number reported as trace		1
Range	T	T	Range		T–0.001
TDE			**LEPTOPHOS**		
Average	T		Average		T
Positive composites			Positive composites		
Total number	1		Total number		1
Number reported as trace	1		Number reported as trace		0
Range	T		Range		0.005
PARATHION			**PCA**		
Average	T		Average	T	
Positive composites			Positive composites		
Total number	1		Total number	1	
Number reported as trace	1		Number reported as trace	0	
Range	T		Range	0.003	
LEAD			**PCP**		
Average	0.04	0.08	Average	T	
Positive composites			Positive composites		
Total number	6	10	Total number	1	
Number reported as trace	3	5	Number reported as trace	0	
Range	0.10–0.18	0.10–0.22	Range	0.01	
LINDANE			**ARSENIC**		
Average		T	Average	T	
Positive composites			Positive composites		
Total number		7	Total number	1	
Number reported as trace		4	Number reported as trace	1	
Range		0.001–0.002	Range	T	
VIII. FRUIT AND FRUIT JUICES					
ZINC			**DIAZINON**		
Average	1.1	1.6	Average		T
Positive composites			Positive composites		
Total number	10	10	Total number		1
Number reported as trace	0	0	Number reported as trace		0
Range	0.6–1.8	0.7–3.1	Range		0.001
BOTRAN			**CIPC**		
Average	0.002	0.004	Average		0.012
Positive composites			Positive composites		
Total number	3	4	Total number		1
Number reported as trace	0	0	Number reported as trace		0
Range	0.001–0.013	0.003–0.024	Range		0.120
ARSENIC			**CADMIUM**		
Average	T	T	Average	T	T
Positive composites			Positive composites		
Total number	2	2	Total number	1	2
Number reported as trace	2	2	Number reported as trace	1	2
Range	T	T	Range	T	T
LEAD			**CARBARYL**		
Average	0.04	0.02	Average	T	T
Positive composites			Positive composites		
Total number	6	4	Total number	1	1
Number reported as trace	3	2	Number reported as trace	1	1
Range	0.10–0.24	T–0.12	Range	T	T
ENDOSULFAN					
Average		T			
Positive composites					
Total number		1			
Number reported as trace		0			
Range		0.006			

(Continued next page)

TABLE 4. (Cont'd). *Levels of residues, by food class, of infant and toddler food composites from 10 United States cities—August 1974–July 1975*

Chemical	Residue, ppm		Chemical	Residue, ppm	
	Infant	Toddler		Infant	Toddler
IX. OILS AND FATS					
ZINC			SELENIUM		
Average	22.4	14.3	Average	T	T
Positive composites			Positive composites		
Total number	3	10	Total number	2	8
Number reported as trace	0	0	Number reported as trace	2	8
Range	20.9–25.3	9.6–18.3	Range	T	T
CADMIUM			DIELDRIN		
Average	0.08	0.02	Average	0.002	T
Positive composites			Positive composites		
Total number	3	10	Total number	2	4
Number reported as trace	0	6	Number reported as trace	1	3
Range	0.07–0.10	0.05–0.08	Range	T–0.006	T–0.003
TOXAPHENE			PCNB		
Average	0.35	0.061	Average	0.01	0.003
Positive composites			Positive composites		
Total number	3	4	Total number	2	4
Number reported as trace	0	1	Number reported as trace	1	1
Range	0.16–0.51	0.10–0.26	Range	T–0.03	0.004–0.016
MALATHION			PCA		
Average	0.12	0.048	Average	0.003	0.006
Positive composites			Positive composites		
Total number	3	6	Total number	1	5
Number reported as trace	0	0	Number reported as trace	0	1
Range	0.09–0.17	0.043–0.125	Range	0.008	0.003–0.030
HCB			PENTACHLOROBENZENE		
Average	0.001	0.001	Average	0.001	0.001
Positive composites			Positive composites		
Total number	1	4	Total number	1	4
Number reported as trace	0	2	Number reported as trace	0	2
Range	0.002	0.006–0.008	Range	0.002	T–0.006
PCB					
Average		T			
Positive composites					
Total number		1			
Number reported as trace		1			
Range		T			
X. SUGAR AND ADJUNCTS					
ZINC			ARSENIC		
Average	1.1	3.9	Average	T	0.02
Positive composites			Positive composites		
Total number	8	10	Total number	1	1
Number reported as trace	0	0	Number reported as trace	1	0
Range	0.2–2.8	0.4–8.6	Range	T	0.16
BHC			LEAD		
Average		T	Average	T	0.02
Positive composites			Positive composites		
Total number		5	Total number	1	3
Number reported as trace		4	Number reported as trace	1	1
Range		T–0.002	Range	T	0.10–0.11
SELENIUM			LINDANE		
Average	T	T	Average		0.002
Positive composites			Positive composites		
Total number	2	6	Total number		9
Number reported as trace	2	6	Number reported as trace		0
Range	T	T	Range		0.001–0.007
MALATHION			CADMIUM		
Average		0.003	Average	T	T
Positive composites			Positive composites		
Total number		3	Total number	1	8
Number reported as trace		1	Number reported as trace	1	8
Range		0.007–0.020	Range	T	T
TDE			DDE		
Average		T	Average		T
Positive composites			Positive composites		
Total number		1	Total number		1
Number reported as trace		1	Number reported as trace		1
Range		T	Range		T
PCP			DIAZINON		
Average		0.009	Average	T	T
Positive composites			Positive composites		
Total number		1	Total number	1	2
Number reported as trace		0	Number reported as trace	1	2
Range		0.09	Range	T	T

(*Continued next page*)

TABLE 4. (Cont'd). *Levels of residues, by food class, of infant and toddler food composites from 10 United States cities—August 1974–July 1975*

Chemical	Residue, ppm		Chemical	Residue, ppm	
	Infant	Toddler		Infant	Toddler
X. SUGAR AND ADJUNCTS *(Cont'd)*					
BOTRAN			CARBARYL		
Average		0.001	Average	T	
Positive composites			Positive composites		
Total number		2	Total number	1	
Number reported as trace		0	Number reported as trace	1	
Range		0.001–0.007	Range	T	
XI. BEVERAGES					
ZINC			LEAD		
Average	0.5	0.8	Average	0.02	T
Positive composites			Positive composites		
Total number	8	9	Total number	3	3
Number reported as trace	0	0	Number reported as trace	2	3
Range	0.1–1.6	0.1–2.1	Range	T–0.14	T
CADMIUM					
Average	T	T			
Positive composites					
Total number	1	2			
Number reported as trace	1	2			
Range	T	T			

NOTE: Average residues are based upon the total number of composites examined, excluding all Trace reportings. It is quite possible that values reported as T can be well below the detection limits of the method for that composite.

found in all 10 market baskets included: zinc, 9.0–18.4 ppm, average 13.9 ppm; selenium, 0.20–0.30 ppm, average 0.23 ppm; malathion, 0.006–0.039 ppm, average 0.17 ppm; and cadmium, all trace levcls. Lead was found in five market baskets, ranging from 0.20 ppm to 0.31 ppm and averaging 0.073 ppm. Diazinon, dieldrin, and lindane residues were also found.

Toddler.—By contrast to the infant diet, this composite included breads, cakes, cookies, macaroni, canned corn, and noodle soup. All 10 market baskets showed the following residues: zinc, 5.4–9.9 ppm, average 8.0 ppm; selenium, 0.14–0.30 ppm, average 0.22 ppm; and cadmium, all trace levels. Malathion, found in nine market baskets, ranged from 0.004 ppm to 0.018 ppm and averaged 0.009 ppm. Lead was reported in four market baskets, ranging from 0.10 ppm to 0.16 ppm and averaging 0.03 ppm. Also found at low levels were diazinon, 0.002–0.003 ppm, average trace; TCNB; and dieldrin.

POTATOES

Infant.—This composite was included in only seven market baskets; no composites were obtained in the western region. Residues reported in all baskets included zinc, 2.10–6.80 ppm, average 3.83 ppm; and cadmium, trace to 0.05 ppm, average 0.01 ppm. Other reportable residues were dieldrin, 0.004–0.005 ppm, average 0.001 ppm; and CIPC, trace to 0.051 ppm, average 0.007 ppm. Trace levels of diazinon, lindane, and lead were also found.

Toddler.—This composite was included in all 10 market baskets of the series. Composites in all 10 baskets contained residues of zinc, ranging from 2.5 ppm to 6.8 ppm and averaging 3.7 ppm, and cadmium ranging from 0.05 to 0.06 ppm and averaging 0.03 ppm. In addition, composites from five baskets contained CICP residues ranging from 0.011 ppm to 0.052 ppm and averaging 0.15 ppm, and dieldrin residues ranging from 0.002 ppm to 0.005 ppm and averaging 0.001 ppm. Lindane, lead, diazinon, and selenium were found only at trace levels.

VEGETABLES

Infant.—A variety of commercially prepared vegetables and vegetable-meat products were composited. Composites from all 10 baskets contained residues of zinc ranging from 3.0 ppm to 7.9 ppm and averaging 4.6 ppm and residues of cadmium ranging from trace to 0.08 ppm and averaging 0.01 ppm. Lead was found in six market baskets, ranging from 0.10 ppm to 0.18 ppm and averaging 0.04 ppm. PCP was found in the composite of one basket at the 0.01 ppm level but with an overall average of 0.001 ppm. DDE was found in composites of two market baskets of 0.002 ppm and 0.011 ppm and averaged 0.001 ppm. Trace amounts of PCA, TDE, diazinon, parathion, and selenium were also found.

Toddler.—Residues found in vegetable composites of all 10 baskets included: zinc, 3.4–6.4 ppm, average 4.4 ppm; lead, 0.10–0.22 ppm, average 0.08 ppm; and cadmium, trace levels. Lindane was found in seven baskets ranging from 0.001 ppm to 0.002 ppm and averaging a trace. Residues of carbaryl, BHC, diazinon, dieldrin, DDE, leptophos, and selenium were also found.

FRUITS AND FRUIT JUICES

Infant.—The infant diet of fruits and fruit juices was rather limited, including in most cases, raw bananas, commercially processed fruits, and a few selected fruit drinks. Zinc levels were highest, ranging from 0.6 ppm to 1.8 ppm and averaging 1.1 ppm in 10 market baskets. Lead, found in six market baskets, from 0.10 ppm to 0.24 ppm, and averaged 0.04 ppm. Other residues found at low levels included botran, average 0.002 ppm, carbaryl, arsenic, and cadmium.

Toddler.—The toddler diet included many fresh fruits and fruit juices. Zinc was found in all market baskets, ranging from 0.7 ppm to 3.1 ppm and averaging 1.6 ppm for the series. Lead was present in composites from four baskets, two at the trace level, 0.10 ppm, and 0.12 ppm, and averaging 0.02 ppm. Botran was found in four baskets ranging from 0.003 ppm to 0.024 ppm and averaging 0.004 ppm. Other residues included arsenic, cadmium, CIPC, diazinon, endosulfan, and carbaryl.

OILS AND FATS

Infant.—Only the northeast region distinguished the infant and toddler diets for this composite, and it differs only in the peanut butter content. The results represent three market baskets, all of which contained residues of the following: zinc, 20.9–25.3 ppm, average 22.4 ppm; toxaphene, 0.16–0.51 ppm, average 0.35 ppm; malathion, 0.09–0.17 ppm, average 0.12 ppm; and cadmium, 0.07–0.10 ppm, average 0.08 ppm. PCNB was found in composites from two market baskets ranging from trace to 0.03 ppm and averaging 0.01 ppm. Selenium was reported at trace levels for two market baskets. Other residues included dieldrin, HCB, PCA, and pentachlorobenzene.

Toddler.—All 10 market baskets contained zinc residues, ranging from 9.6 ppm to 18.3 ppm and averaging 14.3 ppm; and cadmium residues ranging from 0.05 ppm to 0.08 ppm and averaging 0.02 ppm. Trace levels of selenium were found in eight market baskets. Malathion was found in six market baskets, ranging from 0.043 ppm to 0.12 ppm and averaging 0.048 ppm; toxaphene averaged 0.06 ppm in four market baskets, 0.10–0.26 ppm. Five of the 10 baskets exhibited PCA residues ranging from 0.003 ppm to 0.030 ppm and averaging 0.006 ppm. The remaining residues included HCB, dieldrin, and pentachlorobenzene. A trace of PCB was reported in one composite.

SUGAR AND ADJUNCTS

Infant.—Sugar and either syrup, fruit topping, or jelly were composited. Zinc was the only quantifiable residue, found in eight market baskets; residues ranged from 0.2 to 2.8 ppm, and averaged 1.1 ppm. Trace residues of arsenic, lead, selenium, cadmium, carbaryl, and diazinon were found.

Toddler.—In addition to items on the infant diet, this composite contained jello desserts and assorted candies, including chocolate. Zinc was found in all 10 market baskets, ranging from 0.4 ppm to 8.6 ppm, and averaging 3.9 ppm; lindane was reported for nine market baskets, ranging from 0.001 ppm to 0.007 ppm and averaging 0.002 ppm. A trace of cadmium was found in eight composites and a trace of selenium was found in six composites. One composite contained 0.16 ppm arsenic, and another contained 0.09 ppm PCP. Lead was found in three composites, with results of trace, 0.10 ppm, 0.11 ppm, and averaging 0.02 ppm. Trace amounts of BHC, malathion, DDE, TDE, diazinon, and botran were found.

BEVERAGES

Infant.—A marked difference in the regional diet of the infant resulted in an unusual combination of items. One region had no specific infant diet, another had the same diet for infant and toddler, and of the other two regions, one had cola and brewed tea, and the other had fruit soda. Zinc was reported in eight of the 10 market baskets, ranging from 0.1 ppm to 1.6 ppm and averaging 0.5 ppm. The only other residue reported was lead, in three market baskets, ranging from trace to 0.14 ppm and averaging 0.02 ppm. A trace of cadmium was found in one composite.

Toddler.—Residues were the same as those reported for infant food composites.

Discussion

Table 5 provides a general overview of the results of the survey. It identifies the classes of residues and the number of compounds within the class that were found in each food category.

TABLE 5. *Types and number of residues, by food class, found in infant and toddler total diet samples from 10 United States cities—August 1974–July 1975*

Type of Residue	Food Class [1]											
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	Total
INFANT												
Metals	2	2	4	6	4	3	5	4	3	5	3	41
Pesticides	—	5	6	8	4	3	4	2	4	2	—	38
Fungicides	—	—	—	—	—	1	1	—	2	—	—	4
Industrial chemicals	—	—	—	1	—	—	—	—	1	—	—	2
Herbicides	—	—	—	—	—	—	1	—	—	—	—	1
Total	2	7	10	15	8	7	11	6	10	7	3	86
TODDLER												
Metals	2	2	5	6	4	4	4	4	3	5	3	42
Pesticides	—	5	10	10	3	3	7	5	4	7	—	54
Fungicides	—	—	—	—	1	1	—	1	2	—	—	5
Industrial chemicals	—	—	—	1	—	—	—	—	2	—	—	3
Herbicides	—	—	—	—	—	—	—	—	—	1	—	1
Total	2	7	15	17	8	8	11	10	11	13	3	105

[1] See key in table 1.

INFANT

A total of 306 residues was found in the infant food composites of the 10 market baskets. The compounds, categorized by predominant usage, were as follows: 199 or 65 percent were heavy metals, 99 or 32.3 percent were pesticides, and 2.7 percent included five fungicides, one herbicide, and 2 industrial chemicals.

The heavy metals included zinc, cadmium, selenium, lead, mercury, and arsenic. The most prevalent of these was zinc which ranged from 0.1 ppm to 41.8 ppm in 92 composites. Cadmium, the second most frequently reported heavy metal residue, was found in 41 composites, predominantly in grain and cereal products, potatoes, vegetables, and the meat, fish, and poultry composites. Selenium was found in all meat and all grain composites, and in two or three of each of the whole milk, dairy, vegetables, oils and fats, and sugar composites; none was found in the water, potato, fruit, or beverage composites. Lead was found mostly in the vegetable, fruit, grain composites, and to a lesser extent in the dairy, meat, sugar, and beverage composites; no residue were reported in the water, whole milk, and fats composites. The only positive report for mercury was in the meat composite. Arsenic was found in two fruit composites and in only one composite each of meat, vegetables, and sugar. Tables 2 and 4 show the levels and distributions of the residues.

The 99 pesticide residues can be separated into three types: organochlorines, 76 residues; organophosphates, 21 residues; and two carbaryl residues. Of the organochlorine residues, dieldrin was reported in 20 composites, ranging from 0.001 ppm to 0.006 ppm, but toxaphene was reported in three oil and fat composites at much higher levels, ranging from 0.16 ppm to 0.51 ppm. The organophosphate malathion was found in all 10 grain composites and in three infant oil and fat composites ranging from 0.006 ppm to 0.17 ppm. Carbaryl, the only carbamate screened, was found only twice: once in the fruit composite and once in the sugar composite, both at the trace level.

Five fungicide residues were found: PCNB was found in two oil and fat composites, and its metabolite PCA was found in one vegetable composite. The fungicide residues ranged from trace to 0.03 ppm. CIPC was found in one potato composite at 0.051 ppm.

The herbicide PCP was found in one vegetable composite at a level of 0.01 ppm.

Two industrial chemicals were reported. A trace of PCB was reported in one meat, fish, and poultry composite, and 0.002 ppm pentachlorobenzene was reported in one oil and fat composite.

TODDLER

A total of 477 residues was found in the toddler food composites of the 10 market baskets as follows: 258 or 54.1 percent were heavy metal residues; 196 or 41 percent were pesticide residues; 16 or 3.3 percent were fungicide residues, and 1.6 percent included six industrial chemical residues and one herbicide residue.

The heavy metals included zinc, cadmium, selenium, lead, arsenic, and mercury. Zinc accounted for 105 residues ranging from 0.1 ppm to 41.4 ppm and was found in almost all composites of every market basket. Cadmium was found in 61 composites, 50 of which were at the trace level, ranging from 0.05 ppm to 0.08 ppm; no cadmium was found in milk composites. Selenium was found in 44 composites, ranging from 0.14 ppm to 0.34 ppm; none was found in water, fruit and fruit juices, or the beverage composites.

Lead residues ranging from 0.10 ppm to 0.22 ppm were found in 31 composites; none was found in water, milk, or oil and fat composites. Arsenic, reported in five of the meat composites, two of the fruit, one of the dairy, and one of the sugar composites, ranged from 0.10 ppm to 0.18 ppm. Mercury was found in eight meat composites: seven at trace, one at 0.020 ppm.

Separation of the types of pesticide residues shows 162 organochlorine residues, 32 organophosphate residues, and 2 carbaryl residues. Just as in the infant composites, dieldrin was the most frequently reported organochlorine, with 34 positive findings at levels between 0.001 ppm and 0.007 ppm, whereas toxaphene was reported in four oil and fat composites, with one at trace level and the other three between 0.100 ppm and 0.26 ppm. Malathion was the organophosphate most frequently reported and at the highest level in 18 composites at levels of 0.004–0.025 ppm. Carbaryl was reported in two composites, one vegetable and one fruit, once at trace and once at the 0.001 ppm level.

The finding of 16 fungicide residues in the toddler diet is significant. Three chlorinated fungicides accounted for most of the residues: CIPC was found in five potato composites and one fruit composite ranging from 0.011 ppm to 0.120 ppm; PCNB was found in four oil and fat composites at levels of 0.004–0.016 ppm.

No chlorophenoxy acid herbicides were reported except PCP, found in one sugar composite at 0.09 ppm.

Two industrial chemicals were detected: pentachlorobenzene was found in four oil and fat composites at levels of trace to 0.006 ppm, and a PCB, Aroclor 1254, was found in one meat, fish, and poultry composite and in one oil and fat composite, both at trace levels.

Recovery studies were performed with each market basket, wherein composites were fortified with known compounds within each class of residue and, after corrections were made based on the unfortified composite contribution, calculations were made to determine the percentage of recovery. These results are included in Table 6.

TABLE 6. *Recovery data on residues, found in infant and toddler total diet samples from 10 United States cities—August 1974–July 1975*

Residue	Type of Food Composite	Spike Level, ppm	Range of Blank Level, ppm [1]	Range of Total Found, ppm [1]	No. of Recovery Studies
HCB	Fatty	0.001	0.000	0.0007	1
	Nonfatty	0.001	0.000	0.0004–0.0005	2
Mirex	Fatty	0.05	0.000	0.017	1
	Nonfatty	0.05	0.000	0.01–0.035	2
Leptophos	Fatty	0.05	0.000	0.044	1
	Nonfatty	0.05	0.000	0.024–0.041	2
Carbaryl	Nonfatty	0.20	0.00	0.15–0.20 (0.19)	16
Orthophenyl-phenol	Nonfatty	0.40	0.00	0.20–0.40 (0.32)	17
MCP	Fatty	0.02	0.00	0.0–0.015 (0.0055)	4
	Nonfatty	0.02	0.00	0.014–0.024 (0.018)	8
2,4-DB	Fatty	0.02	0.00	0–0.023 (0.009)	4
	Nonfatty	0.02	0.00	0.004–0.027 (0.017)	4
2,4,5-T	Fatty	0.02	0–0.002 (0.0007)	0.009–0.020 (0.013)	3
	Nonfatty	0.02	0.000	0.003–0.019 (0.016)	5
2,4-D	Fatty	0.02	0.000	0.011–0.014 (0.013)	2
	Fatty	0.04	0.000	0.010–0.020 (0.015)	2
	Nonfatty	0.02	0.000	0.008–0.018 (0.014)	4
	Nonfatty	0.04	0.000	0.004–0.042 (0.023)	4
PCP	Fatty	0.02	0	0.007	1
	Nonfatty	0.02	0–0.002 (0.0005)	0.014–0.020 (0.016)	4
2,4,5-TP	Fatty	0.04	0.000	0.022–0.074 (0.048)	2
	Nonfatty	0.04	0.000	0.013–0.039 (0.030)	4
BBHC	Fatty	0.02	0.000	0.010–0.019 (0.015)	2
	Nonfatty	0.02	0.000	0.017–0.018 (0.018)	4
CIPC	Nonfatty	0.05	0	0.036–0.070 (0.048)	3
Dieldrin	Fatty	0.01	0.0010–0.0068 (0.0029)	0.0105–0.0176 (0.0129)	3
	Nonfatty	0.005	0	0.004–0.0071 (0.0057)	6
Methyl parathion	Nonfatty	0.005	0	0.0023–0.0057 (0.0038)	5
Ronnel	Fatty	0.005	0	0.0030–0.0035 (0.0032)	2
	Nonfatty	0.005	0	0.0032–0.0052 (0.0045)	4
Oxychlordane	Fatty	0.005	0	0.0020–0.0021	2
	Nonfatty	0.003	0	0.0019–0.0034 (0.0027)	4
Parathion	Fatty	0.005	0	0.0041–0.0053	2
	Nonfatty	0.005	0	0.0044–0.0049 (0.0046)	4
Endrin	Fatty	0.01	0	0.0086–0.011	2
	Nonfatty	0.01	0	0.0082–0.0104 (0.0094)	4
Arsenic	Fatty	0.30	0.01–0.066 (0.0160)	0.205–0.340 (0.294)	10
	Nonfatty	0.30	0.005–0.065 (0.017)	0.205–0.415 (0.327)	20

(*Continued*)

TABLE 6. (Cont'd).

Residue	Type of Food Composite	Spike Level ppm	Range of Blank Level, ppm [1]	Range of Total Found, ppm [1]	No. of Recovery Studies
Cadmium	Fatty	0.10	0.001–0.068 (0.020)	0.099–0.155 (0.052)	20
	Nonfatty	0.10	0.001–0.081 (0.019)	0.092–0.174 (0.118)	20
Lead	Fatty	0.20	0.000–0.056 (0.012)	0.113–0.296 (0.204)	10
	Nonfatty	0.20	0.000–0.160 (0.058)	0.108–0.381 (0.245)	20
Mercury	Fatty	0.06	0.000–0.013 (0.002)	0.051–0.073 (0.057)	9
	Nonfatty	0.06	0.000–0.002 (0.0006)	0.056–0.071 (0.061)	9
	Nonfatty	0.03	0.000	0.024–0.031 (0.028)	3
Selenium	Fatty	0.20	0.01–0.17 (0.05)	0.07–0.31 (0.21)	10
	Nonfatty	0.20	0.00–0.28 (0.045)	0.09–0.63 (0.22)	18
Zinc	Fatty	5.0	3.0–4.9 (4.19)	7.7–12.5 (9.94)	3
	Fatty	25.0	2.5–23.2 (14.7)	26.0–45.0 (37.9)	3
	Nonfatty	5.0	0.0–6.40 (2.52)	3.40–14.0 (7.38)	17

[1] Numbers in parentheses represent average residue levels.

LITERATURE CITED

(*1*) *Association of Official Analytical Chemists. 1975.* Official Methods of Analysis, 12th ed., Washington, D.C. Sections 25.026–25.030.

(*2*) *Association of Official Analytical Chemists. 1975.* Official Methods of Analysis, 12th ed., Washington, D.C. Sections 25.0065–25.070.

(*3*) *Association of Official Analytical Chemists. 1975.* Official Methods of Analysis, 12th ed., Washington, D.C. Sections 25.103–25.105.

(*4*) *Association of Official Analytical Chemists. 1975.* Official Methods of Analysis, 12th ed., Washington, D.C. Sections 25.117–25.120.

(*5*) *Association of Official Analytical Chemists. 1975.* Official Methods of Analysis, 12th ed., Washington, D.C. Sections 25.143–25.147.

(*6*) *Finocchiaro, J. M., and W. R. Benson. 1965.* Thin-layer chromatographic determination of carbaryl (Sevin) in some foods. J. Assoc. Off. Agric. Chem. 48(4):736–738.

(*7*) *Food and Drug Administration. 1971.* Pesticide Analytical Manual, Vol. I and II. U.S. Department of Health, Education, and Welfare, Washington, D.C.

(*8*) *Food and Drug Administration. 1976.* Compliance Program Guidance Manual. Section 7305.002, Part IV, B, 4, a, 2(a).

(*9*) *Hundley, H. K., and J. C. Underwood. 1970.* Determination of total arsenic in total diet samples. J. Assoc. Off. Anal. Chem. 53(6):1176–1178.

(*10*) *Johnson, R. D., and D.D. Manske. 1975.* Pesticide residues in total diet samples (IX). Pestic. Monit. J. 9(4):157–169.

(*11*) *Johnson, R. D., and D. D. Manske. 1977.* Pesticide and other chemical residues in total diet samples (XI). Pestic. Monit. J. 11(3):116–131.

(*12*) *Porter, M. L., R. J. Gajan, and J. A. Burke. 1969.* Acetonitrile extraction and determination of carbaryl in fruits and vegetables. J. Assoc. Off. Anal. Chem. 52(1):177–181.

FISH, WILDLIFE, and ESTUARIES

Organochlorine Pesticide Residues in Animals of Tasmania, Australia—1975–77

Harry Bloom,[1] Walter Taylor,[2] Walter R. Bloom,[3] and Geoffrey M. Ayling[4]

ABSTRACT

Animals taken in Tasmania including duck (Anas superciliosa), *eel* (Anguilla australis), *English perch* (Perca fluviatilis), *white-faced heron* (Ardea pacifica), *brown trout* (Salmo trutta), *European starling* (Sturnus vulgaris), *cat* (Felis cattus), *cormorant* (Phalacrocorax *sp.*), *mutton bird* (Puffinus tenuirostris), *Tasmanian devil* (Sarcophilus harrisii), *rainbow trout* (Salmo gairdnerii), *Tasmanian raven* (Corvus mellori), *tench* (Tinca tinca), *and quail* (Coturnix *sp.*) *were sampled for* p,p'-*DDE,* p,p'-*TDE,* p,p'-*DDT, lindane, dieldrin, and hexachlorobenzene. Pesticide residue levels exceeded 0.1 ppm in at least one animal from each area and in the majority of animals sampled from all areas. Pesticide sources could not be determined, partly because migratory species such as ducks, mutton birds, cormorants, and eels may have ingested pesticides outside of Tasmania.*

Introduction

Organochlorine pesticides have been used widely in Tasmania, Australia to control agricultural pests. In particular, dieldrin has been used to mothproof woolens manufactured in northern Tasmania. Restrictions on permissible levels of pesticide residues in agricultural products exported to Europe and the United States have resulted in a considerable decrease in pesticide use. However, pesticides are still available for nonagricultural and other domestic purposes.

In a preliminary study in this program, analyses of fatty tissues of several animals from Macquarie Island (near Antarctica) showed surprising concentrations of the following organochlorines:

Species	Residues, ppm HCB	Lindane	Dieldrin	ΣDDT
Gentoo penguin (*Pygoseelis papua*)	0.44	0.03	0.03	3.4
Royal penguin (*Eudyptes schlegeli*) (1)	0.08	0.01	0.02	0.47
(2)	0.16	0.01	0.02	0.41
Rockhopper penguin (*Eudyptes chrysocomi*) (1)	0.11	—	0.01	0.54
(2)	0.14	0.01	0.04	0.43
Weka (*Gallirallus australis*)	0.08	0.01	—	0.66
Macquarie Island cormorant (*Phalacrocorax albiventer*)	0.12	0.01	0.01	0.76
King penguin (*Aptenodytes patagonica*)	0.03	0.01	0.01	0.15

Researchers in other countries have studied the bioconcentration of DDT in the environment (*1*); the movement of ΣDDT into the atmosphere (*7*), which appears to be an important mode of transport of residues; pesticide residues in the Canadian Great Lakes region (*5*); the role of marine phytoplankton as a transport medium (*3*); the effects of DDT on reproduction of higher animals (*9*); and the physiological and biological effects of pesticides on poultry (*4*).

Because there had been no previous survey of pesticide residues in Tasmanian wildlife, the need existed for a study to determine whether pesticide concentrations in Tasmania were similar to those throughout the world.

Sample Collection

Animals were taken during 1975–77 throughout Tasmania, Australia (Fig. 1) by officers of the Tasmanian National Parks and Wildlife Service, Tasmanian Inland Fisheries Commission, and the Victoria Museum, Launceston, Tasmania. Although a sampling program was initially established, problems of logistics, manpower, the distribution of the various species, and weather made it necessary in the long term to sample animals which were readily accessible at the particular time and locality. Thus the initial aim of collecting animals high in the food chain was not entirely

[1] Chemistry Department, The University of Tasmania, Hobart, Tasmania, Australia.

[2] Government Analyst's Laboratory, Campbell St., Hobart, Tasmania, Australia.

[3] School of Mathematical and Physical Sciences, Murdoch University, Perth, Western Australia.

[4] State Department of the Environment, Hobart, Tasmania, Australia.

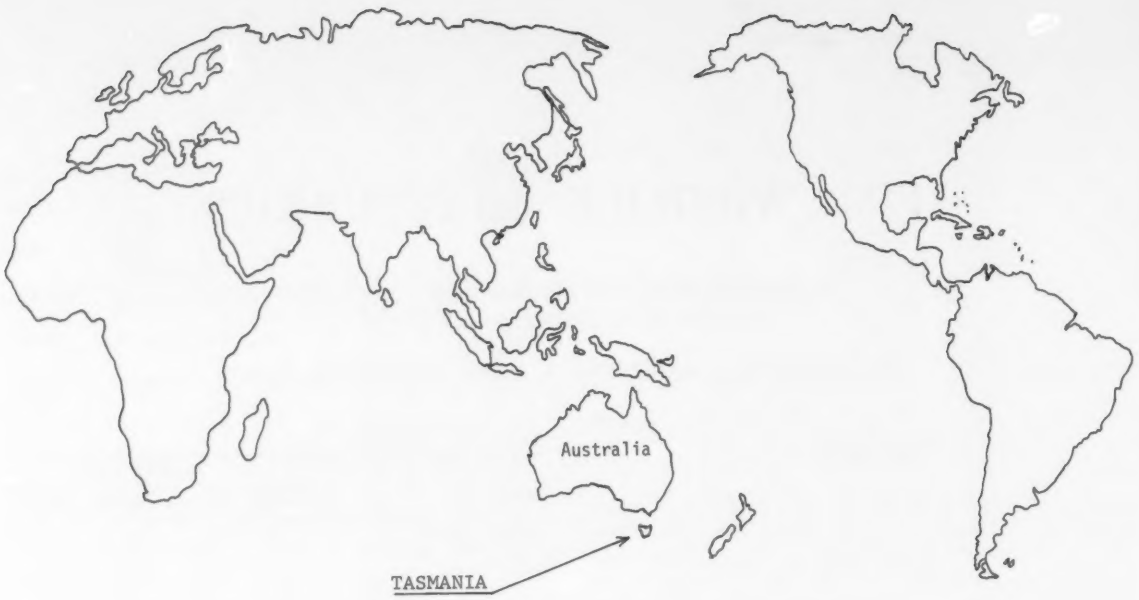

FIGURE 1. *World map showing location of Tasmania, Australia*

achieved. For similar reasons, all species could not be collected from all areas of Tasmania.

Locations from which animals were taken are shown in Figure 2. Species are listed in Table 1.

Analytical Procedures

SAMPLE PREPARATION

The sampled species, although differing widely in type, did not present any unusual problems in cleanup of residue for analysis.

Fat was extracted from the adipose tissue of ducks, Tasmanian devils, and cats by solution in hexane, and the solution was filtered through anhydrous sodium sulfate. The solvent was removed on a warm water bath. The extracted fat was cleaned on an alumina minicolumn (*6*).

Fish were macerated and extracted with a mixture of hexane–acetone–diethyl ether. The extracted fat was cleaned on an alumina minicolumn.

Birds were dissected, and the liver and breast tissue were analyzed separately following initial acetonitrile extraction of the homogenate. The extract was filtered through cotton wool and extracted by reverse-phase partition chromatography into hexane. The hexane extract was in turn concentrated and cleaned on an alumina minicolumn.

GAS-LIQUID CHROMATOGRAPHY (GLC)

Analyses were performed on a Tracor Model MT 220 gas chromatograph equipped with a Ni^{63} electron-capture detector. Instrument parameters and operating conditions follow:

Columns:	glass 6 ft long × ¼ inch OD, packed with a mixture of 2 percent OV–101 and 3 percent QF–1, or 3 percent OV–101, on 100–120-mesh Gas-Chrom Q
Temperatures:	injection port 225°C column oven 200°C detector 275°C
Carrier gas:	nitrogen flowing at 60 ml/minute
Purge gas:	nitrogen flowing at 20 ml/minute

Quantitation was based on comparison with peak heights obtained by injecting known amounts of pesticides. Pesticide identity was confirmed by comparison of p-values (*2*) for several solvent systems, GLC retention values on two columns of differing polarity, and derivative formation.

All samples were analyzed for hexachlorobenzene (HCB), lindane, dieldrin, *p,p'*-DDE, *p,p'*-TDE, and *p,p'*-DDT.

Organochlorine pesticide standards of greater than 99 percent purity were obtained from various sources. Recovery rates were 90–100 percent but were usually close to 100 percent, hence correction for recovery was not necessary.

Results and Discussion

In every area at least one animal contained a pesticide residue level exceeding 0.1 ppm, and for most areas this was true for the majority of animals sampled. Pesticide sources could not be determined, partly because migratory species such as ducks, mutton birds, cormorants, and eels may have ingested pesticides outside of Tasmania.

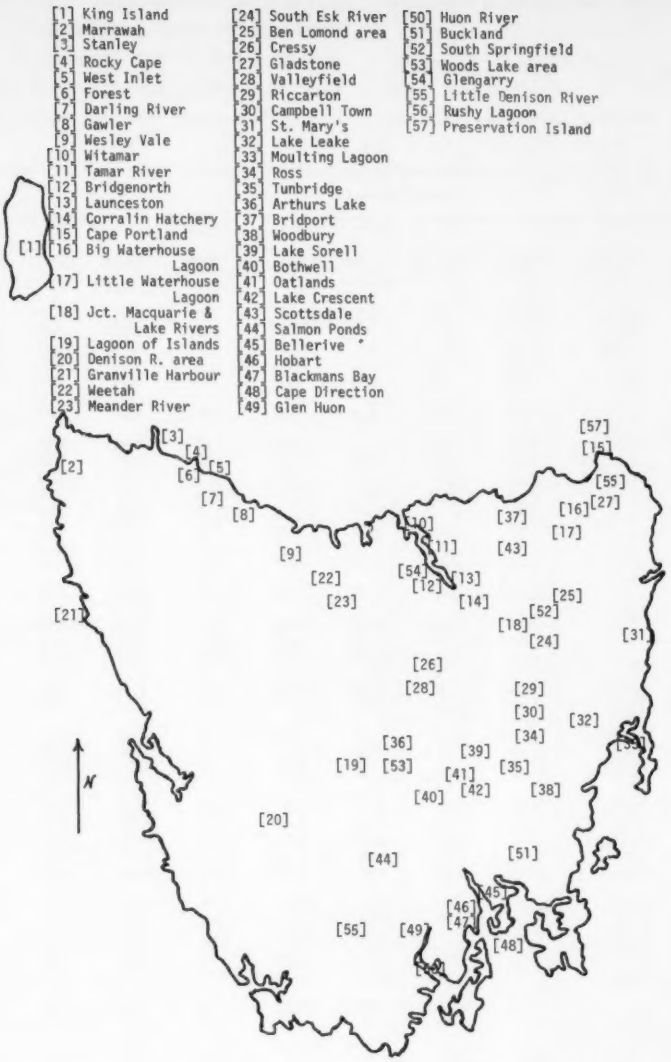

FIGURE 2. *Locations in Tasmania, Australia, where various animals were obtained for organochlorine pesticide residue analysis, 1975–77*

TABLE 1. *Species collected in Tasmania, Australia, for organochlorine pesticide residue analyses, 1975–77*

Common Name	Scientific Name
Duck	*Anas superciliosa*
Eel	*Anguilla australis*
English perch	*Perca fluviatilis*
White-faced heron	*Ardea pacifica*
Brown trout	*Salmo trutta*
European starling	*Sturnus vulgaris*
Cat	*Felis cattus*
Cormorant	*Phalacrocorax sp.*
Mutton bird	*Puffinus tenuirostris*
Tasmanian devil	*Sarcophilus harrisii*
Rainbow trout	*Salmo gairdnerii*
Tasmanian raven	*Corvus mellori*
Tench	*Tinca tinca*
Quail	*Coturnix* sp.

To isolate any one area as having a significantly higher level of pesticide than other areas it would be desirable to have readings for several of the 14 animals, both in the area and elsewhere. The difficulty in obtaining samples in all areas precluded such a plan; in most cases only one species was sampled in any single area. Also, there is a large variety of sample sizes: from one Tasmanian devil in Granville Harbour to 37 ducks in Ross.

Wide fluctuations in the results for most species made the use of means and standard deviations of little value, e.g., for ducks from Cressy (area 26) the mean level

of ΣDDT was 32.07 ppm, and the standard deviation was 74.49 ppm.

The data here are characteristic of similar experiments. Many readings are clustered in a small range, here 0.0–0.2 ppm with a few outlying points as high as 321.0 ppm. When more than seven animals of the same species were sampled from the same area, the data in Table 2 were summarized as maximum, upper quartile, median, lower quartile, or minimum. Where fewer than seven animals were sampled, all data are

TABLE 2. *Summary of data on organochlorine pesticide residues in animals of Tasmania, Australia—1975–77*[1]

			Residues, ppm							
Area	Species	Range	HCB	Lindane	DDE	Dieldrin	TDE	DDT	ΣDDT	Samples
[1]	Cat									
		MAX.	0.50	0.40	9.80	3.90	1.40	5.40	15.20	20
		U.Q.	0.10	0.01	5.55	0.50	0.50	2.45	8.00	
		MED.	0.01	0.00	4.55	0.30	0.35	2.00	6.45	
		L.Q.	0.00	0.00	2.45	0.05	0.10	1.50	4.90	
		MIN.	0.00	0.00	0.30	0.00	0.00	0.40	0.80	
[2]	Duck		0.00	0.50	0.10	0.10	0.00	0.00	0.10	1
[3]	Duck		0.00	0.10	0.20	0.10	0.00	0.00	0.20	
			0.00	0.20	1.70	0.20	0.00	0.30	2.00	
			0.00	0.10	1.20	0.00	0.00	0.20	1.40	6
			0.00	0.01	1.00	0.90	2.00	2.60	5.60	
			0.00	0.10	0.01	0.10	0.00	0.00	0.01	
			0.00	0.00	0.60	0.01	0.10	0.01	0.70	
[4]	Duck		0.00	0.01	0.90	0.00	0.00	0.20	1.10	1
[5]	Duck		0.00	0.01	1.30	0.20	0.00	0.20	1.50	1
[6]	Duck		0.00	0.01	8.10	0.00	0.00	2.20	10.30	3
			0.00	0.01	1.20	0.01	0.00	0.30	1.50	
			0.00	0.01	0.60	0.10	0.00	0.40	1.00	
[7]	Brown trout	MAX.	0.00	0.20	0.90	0.50	1.20	1.60	3.60	23
		U.Q.	0.00	0.10	0.70	0.10	0.20	0.10	0.95	
		MED.	0.00	0.10	0.40	0.10	0.20	0.00	0.60	
		L.Q.	0.00	0.01	0.40	0.01	0.10	0.00	0.50	
		MIN.	0.00	0.00	0.01	0.00	0.00	0.00	0.01	
[8]	English perch	MAX.	0.20	0.50	8.40	1.50	5.50	1.50	14.10	30
		U.Q.	0.10	0.30	3.00	0.90	3.80	0.80	7.00	
		MED.	0.01	0.20	2.10	0.75	2.80	0.50	5.75	
		L.Q.	0.00	0.20	1.60	0.70	2.30	0.40	4.70	
		MIN.	0.00	0.10	0.90	0.50	1.30	0.10	2.80	
[9]	Eel	MAX.	0.00	0.60	8.20	6.00	6.20	18.30	32.70	29
		U.Q.	0.00	0.10	1.90	0.70	1.00	1.20	3.80	
		MED.	0.00	0.01	1.10	0.60	0.70	0.80	2.90	
		L.Q.	0.00	0.01	0.80	0.40	0.50	0.60	2.10	
		MIN.	0.00	0.01	0.30	0.00	0.30	0.40	1.20	
[10]	Cat		0.00	0.00	1.80	0.01	0.00	0.00	1.80	2
			0.00	0.00	0.70	0.01	0.00	0.00	0.70	
[11]	Rainbow trout		0.00	0.00	2.70	3.70	0.00	0.90	3.60	4
			0.00	0.00	1.60	2.40	0.00	0.50	2.10	
			0.00	0.00	0.10	0.20	0.00	0.20	0.30	
			0.00	0.00	0.10	0.20	0.00	0.10	0.20	
[12]	Cat		0.00	0.00	0.80	0.20	0.10	0.20	1.10	1
[13]	Cat		0.00	0.00	1.90	4.30	0.01	0.50	2.40	1
[14]	Tench		0.01	0.01	0.10	1.70	0.00	0.00	0.10	2
			0.00	0.00	0.01	0.00	0.00	0.00	0.01	
[15]	Duck		0.00	0.00	9.60	0.00	4.20	24.00	37.80	1
[15]	Tasmanian raven		0.00	0.00	0.00	0.00	0.00	0.00	0.00	1
[16]	Duck	MAX.	0.10	0.00	3.60	0.70	0.01	0.80	4.40	9
		U.Q.	0.10	0.00	1.40	0.10	0.00	0.50	1.85	
		MED.	0.00	0.00	0.70	0.00	0.00	0.10	0.70	
		L.Q.	0.00	0.00	0.30	0.00	0.00	0.00	0.35	
		MIN.	0.00	0.00	0.10	0.00	0.00	0.00	0.10	
[16]	Eel		0.20	1.30	0.80	0.30	1.20	0.20	2.20	6
			0.10	0.60	0.70	0.30	0.60	0.20	1.50	
			0.00	0.10	0.60	0.01	0.40	0.20	1.20	
			0.00	0.10	0.40	0.00	6.40	0.00	6.80	
			0.00	0.10	0.60	0.00	0.80	0.20	1.60	
			0.00	0.00	0.70	0.00	0.50	0.10	1.30	

(Continued next page)

TABLE 2. (Cont'd.) *Summary of data on organochlorine pesticide residues in animals of Tasmania, Australia—1975–77*

Area	Species	Range	Residues, ppm							
			HCB	Lindane	DDE	Dieldrin	TDE	DDT	ΣDDT	Samples
[17]	Eel		0.00	0.00	0.10	0.00	0.00	0.00	0.10	5
			0.00	0.01	0.00	0.00	0.00	0.00	0.00	
			0.01	0.01	0.10	0.00	0.00	0.00	0.10	
			0.00	0.01	0.10	0.00	0.00	0.00	0.10	
			0.00	0.01	0.00	0.00	0.00	0.00	0.00	
[17]	Cormorant		0.01	0.01	0.10	0.00	0.00	0.00	0.10	1
[18]	Eel	MAX.	0.00	0.20	1.20	0.60	0.40	0.70	2.30	15
		U.Q.	0.00	0.10	0.25	0.35	0.10	0.10	0.40	
		MED.	0.00	0.10	0.20	0.30	0.10	0.10	0.40	
		L.Q.	0.00	0.10	0.20	0.25	0.00	0.10	0.40	
		MIN.	0.00	0.10	0.00	0.00	0.00	0.00	0.00	
[19]	Tasmanian devil		0.10	0.01	0.50	0.01	0.00	0.01	0.50	1
[20]	Tasmanian devil		0.01	0.01	0.01	0.01	0.01	0.01	0.01	2
			0.01	0.01	0.01	0.01	0.01	0.01	0.01	
[21]	10		0.10	0.01	0.10	0.10	0.10	0.10	0.30	1
[22]	8		0.00	0.01	0.01	0.00	0.00	0.00	0.01	3
			0.00	0.01	0.01	0.00	0.00	0.00	0.01	
			0.01	0.01	0.01	0.00	0.00	0.00	0.01	
[23]	Duck	MAX.	0.00	0.01	7.60	0.30	0.80	0.80	7.70	10
		U.Q.	0.00	0.01	0.80	0.10	0.00	0.10	1.60	
		MED.	0.00	0.01	0.55	0.01	0.00	0.10	0.60	
		L.Q.	0.00	0.00	0.20	0.00	0.00	0.00	0.30	
		MIN.	0.00	0.00	0.10	0.00	0.00	0.00	0.20	
[24]	Brown trout		0.00	0.10	0.20	0.10	0.10	0.10	0.40	5
			0.00	0.10	0.20	0.01	0.01	0.01	0.20	
			0.00	0.10	0.20	0.10	0.01	0.10	0.30	
			0.00	0.01	0.20	0.01	0.10	0.10	0.40	
			0.00	0.01	0.20	0.10	0.10	0.10	0.40	
[24]	Tench	MAX.	0.60	8.80	0.60	0.80	0.00	0.00	0.60	12
		U.Q.	0.10	2.75	0.30	0.60	0.00	0.00	0.30	
		MED.	0.10	2.05	0.20	0.20	0.00	0.00	0.20	
		L.Q.	0.00	1.75	0.20	0.20	0.00	0.00	0.20	
		MIN.	0.00	1.10	0.20	0.10	0.00	0.00	0.20	
[25]	Tasmanian devil		0.01	0.01	0.01	0.01	0.01	0.01	0.01	1
[26]	Duck		0.00	0.00	1.90	0.00	0.00	0.00	1.90	6
			0.00	0.00	0.30	0.00	0.00	0.00	0.30	
			0.00	0.00	0.20	0.00	0.00	0.10	0.30	
			5.20	2.60	57.30	18.30	56.60	70.20	184.10	
			0.00	0.00	2.60	0.10	0.00	0.30	2.90	
			0.00	0.00	0.80	0.00	0.10	2.00	2.90	
[26]	Tasmanian raven	MAX.	0.00	0.01	1.10	0.01	0.01	0.00	1.10	16
		U.Q.	0.00	0.01	0.30	0.00	0.00	0.00	0.30	
		MED.	0.00	0.00	0.10	0.00	0.00	0.00	0.10	
		L.Q.	0.00	0.00	0.01	0.00	0.00	0.00	0.01	
		MIN.	0.00	0.00	0.01	0.00	0.00	0.00	0.01	
[27]	Duck		0.00	0.00	0.01	0.00	0.00	0.00	0.01	3
			0.00	0.00	0.60	0.00	0.00	0.20	0.80	
			0.00	0.00	25.80	0.00	0.00	9.00	34.80	
[28]	Duck		0.00	0.00	0.10	0.00	0.00	0.00	0.10	2
			0.00	0.00	0.01	0.01	0.00	0.00	0.01	
[29]	Duck		0.00	0.00	0.10	0.00	0.00	0.00	0.10	1
[30]	Duck		0.00	0.01	0.00	0.00	0.00	0.00	0.00	4
			0.00	0.00	0.01	0.00	0.00	0.00	0.01	
			0.00	0.00	0.40	0.20	0.00	0.00	0.40	
			0.00	0.20	0.10	0.01	0.10	0.10	0.30	
[31]	Cat		0.00	0.00	1.00	0.00	0.00	0.10	1.10	1
[32]	Cormorant		0.00	0.01	0.20	0.00	0.00	0.00	0.20	2
			0.01	0.01	0.20	0.00	0.00	0.00	0.20	
[33]	Duck	MAX.	0.20	0.01	11.20	0.30	0.00	23.70	34.90	26
		U.Q.	0.00	0.00	0.60	0.00	0.00	0.20	1.70	
		MED.	0.00	0.00	0.35	0.00	0.00	0.00	0.40	
		L.Q.	0.00	0.00	0.20	0.00	0.00	0.00	0.20	
		MIN.	0.00	0.00	0.01	0.00	0.00	0.00	0.01	

(Continued next page)

TABLE 2. (Cont'd.) *Summary of data on organochlorine pesticide residues in animals of Tasmania, Australia—1975–77*

Area	Species	Range	Residues, ppm HCB	Lindane	DDE	Dieldrin	TDE	DDT	ΣDDT	Samples
[34]	Duck	MAX.	0.00	0.10	7.00	1.60	0.20	2.60	7.30	37
		U.Q.	0.00	0.01	0.60	0.10	0.00	0.10	1.00	
		MED.	0.00	0.00	0.40	0.01	0.00	0.00	0.40	
		L.Q.	0.00	0.00	0.20	0.00	0.00	0.00	0.20	
		MIN.	0.00	0.00	0.10	0.00	0.00	0.00	0.10	
[34]	White-faced heron		All the readings are zero							5
[34]	Cat	MAX.	0.00	0.00	5.60	0.40	0.60	4.60	9.00	9
		U.Q.	0.00	0.00	4.00	0.30	0.20	3.00	7.55	
		MED.	0.00	0.00	1.50	0.20	0.10	1.70	3.60	
		L.Q.	0.00	0.00	1.00	0.10	0.00	0.80	1.90	
		MIN.	0.00	0.00	0.80	0.10	0.00	0.10	0.90	
[34]	Tasmanian raven	MAX.	0.00	0.00	0.30	0.10	0.01	0.01	0.30	23
		U.Q.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		MED.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		L.Q.	0.00	0.00	0.01	0.00	0.00	0.00	0.01	
		MIN.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
[35]	Duck		0.00	0.01	3.90	0.30	0.00	4.70	8.60	3
			0.00	0.00	0.20	0.00	0.00	0.10	0.30	
			0.00	0.00	5.10	0.30	0.00	4.10	9.20	
[36]	Duck		0.00	0.00	0.20	0.00	0.00	0.00	0.20	4
			0.00	0.00	0.10	0.00	0.00	0.01	0.10	
			0.00	0.00	0.10	0.00	0.00	0.00	0.10	
			0.00	0.00	1.70	0.00	0.00	0.00	1.70	
[37]	Eel	MAX.	0.00	0.00	0.70	0.00	0.00	0.00	0.70	12
		U.Q.	0.00	0.00	0.55	0.00	0.00	0.00	0.55	
		MED.	0.00	0.00	0.30	0.00	0.00	0.00	0.30	
		L.Q.	0.00	0.00	0.20	0.00	0.00	0.00	0.20	
		MIN.	0.00	0.00	0.10	0.00	0.00	0.00	0.10	
[37]	Cormorant		0.00	0.01	0.01	0.00	0.00	0.00	0.01	1
[38]	Duck		0.00	0.00	1.50	0.01	0.00	0.10	1.60	2
			0.00	0.01	0.90	0.00	0.00	0.00	0.90	
[39]	Duck	MAX.	0.00	0.10	127.00	0.01	0.60	133.00	260.00	20
		U.Q.	0.00	0.05	1.10	0.00	0.00	0.35	1.20	
		MED.	0.00	0.00	0.50	0.00	0.00	0.00	0.65	
		L.Q.	0.04	0.00	0.10	0.00	0.00	0.00	0.15	
		MIN.	0.00	0.00	0.01	0.00	0.00	0.00	0.01	
[39]	4		All the readings are zero							5
[39]	Tasmanian raven		0.00	0.00	0.00	0.00	0.00	0.00	0.00	1
[40]	White-faced heron		0.00	0.00	0.00	0.00	0.00	0.00	0.00	1
[40]	European starling	MAX.	0.00	0.01	0.10	0.01	0.00	0.00	0.10	13
		U.Q.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		MED.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		L.Q.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		MIN.	0.00	0.00	0.01	0.00	0.00	0.00	0.01	
[40]	Tasmanian raven		0.00	0.00	0.01	0.01	0.00	0.00	0.01	3
			0.00	0.00	0.01	0.01	0.00	0.00	0.01	
			0.00	0.00	0.01	0.00	0.00	0.00	0.01	
[41]	White-faced heron		0.00	0.00	1.00	0.00	0.00	0.00	0.00	1
[41]	European starling	MAX.	0.00	0.00	0.60	0.01	0.00	0.00	0.60	7
		U.Q.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		MED.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		L.Q.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		MIN.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
[42]	Duck	MAX.	0.00	0.10	6.70	9.60	0.00	1.30	7.90	19
		U.Q.	0.00	0.00	0.85	0.00	0.00	0.05	1.05	
		MED.	0.00	0.00	0.20	0.00	0.00	0.00	0.30	
		L.Q.	0.00	0.00	0.05	0.00	0.00	0.00	0.05	
		MIN.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	.
[42]	White-faced heron		All the readings are zero							2

(Continued next page)

TABLE 2. (Cont'd.) *Summary of data on organochlorine pesticide residues in animals of Tasmania, Australia—1975–77*

Area	Species	Range	Residues, ppm HCB	Lindane	DDE	Dieldrin	TDE	DDT	ΣDDT	Samples
[43]	White-faced heron		0.00	0.00	2.10	0.00	0.00	0.00	2.10	3
			0.00	0.00	0.00	0.00	0.00	0.00	0.00	
			0.00	0.00	0.00	0.00	0.00	0.00	0.00	
[43]	Tasmanian raven		0.00	0.00	0.00	0.00	0.00	0.00	0.00	4
			0.00	0.00	0.00	0.00	0.00	0.00	0.00	
			0.00	0.00	0.01	0.00	0.00	0.00	0.01	
			0.00	0.00	0.01	0.00	0.00	0.00	0.01	
[44]	Cormorant		0.01	0.01	0.20	0.00	0.00	0.00	0.20	1
[45]	European starling									
		MAX.	0.00	0.01	0.40	0.10	0.00	0.00	0.40	19
		U.Q.	0.00	0.00	0.10	0.05	0.00	0.00	0.10	
		MED.	0.00	0.00	0.10	0.01	0.00	0.00	0.10	
		L.Q.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		MIN.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
[46]	White-faced heron		0.00	0.00	0.01	0.00	0.00	0.00	0.01	1
[47]	European starling		0.00	0.00	0.50	0.01	0.00	0.00	0.50	3
			0.00	0.00	0.30	0.10	0.00	0.00	0.30	
			0.00	0.00	0.01	0.01	0.00	0.00	0.01	
[48]	Mutton bird	MAX.	0.01	0.01	0.01	0.01	0.00	0.00	0.01	31
		U.Q.	0.00	0.01	0.01	0.00	0.00	0.00	0.01	
		MED.	0.00	0.01	0.00	0.00	0.00	0.00	0.00	
		L.Q.	0.00	0.01	0.00	0.00	0.00	0.00	0.00	
		MIN.	0.00	0.01	0.00	0.00	0.00	0.00	0.00	
[49]	European starling									
		MAX.	0.00	0.00	8.20	0.01	0.00	0.00	8.20	30
		U.Q.	0.00	0.00	2.20	0.00	0.00	0.00	2.20	
		MED.	0.00	0.00	1.10	0.00	0.00	0.00	1.10	
		L.Q.	0.00	0.00	0.60	0.00	0.00	0.00	0.60	
		MIN.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
[50]	Duck	MAX.	0.00	0.10	136.00	0.20	62.00	321.00	519.00	22
		U.Q.	0.00	0.01	8.00	0.00	0.10	2.20	8.00	
		MED.	0.00	0.00	2.35	0.00	0.00	0.30	3.85	
		L.Q.	0.00	0.00	0.60	0.00	0.00	0.01	0.80	
		MIN.	0.00	0.00	0.20	0.00	0.00	0.00	0.20	
[51]	Cormorant		0.00	0.01	0.10	0.00	0.00	0.00	0.10	3
			0.00	0.00	0.10	0.00	0.00	0.00	0.10	
			0.00	0.00	0.10	0.00	0.00	0.00	0.10	
[52]	Cormorant		0.00	0.01	0.10	0.00	0.00	0.00	0.10	4
			0.00	0.00	0.01	0.00	0.00	0.00	0.01	
			0.00	0.00	0.10	0.00	0.00	0.00	0.10	
			0.00	0.01	0.01	0.00	0.00	0.00	0.01	
[53]	Tasmanian devil		0.01	0.01	0.01	0.10	0.00	0.01	0.01	3
			0.01	0.01	0.01	0.01	0.01	0.01	0.01	
			0.01	0.01	0.01	0.01	0.00	0.01	0.01	
[54]	Tasmanian raven		0.00	0.00	0.00	0.00	0.00	0.00	0.00	1
[55]	Tasmanian devil		0.01	0.00	0.01	0.01	0.01	0.00	0.01	1
[56]	Tasmanian raven		0.00	0.00	0.00	0.00	0.00	0.00	0.00	1
[57]	Quail		0.00	0.01	0.01	0.00	0.00	0.00	0.01	6
			0.00	0.01	0.01	0.00	0.00	0.00	0.01	
			0.00	0.01	0.01	0.00	0.00	0.00	0.01	
			0.01	0.01	0.01	0.00	0.00	0.00	0.01	
			0.01	0.01	0.10	0.01	0.00	0.00	0.10	
			0.01	0.01	0.01	0.01	0.00	0.00	0.01	

NOTE: MAX. = maximum, U.Q. = upper quartile, MED. = median, L.Q. = lower quartile, MIN. = minimum.

[1] The complete set of data can be obtained from Professor H. Bloom, Chemistry Department, The University of Tasmania, G.P.O. Box 252C, Hobart, Tasmania, Australia, 7001. Where fewer than seven animals were sampled, all data are given.

given. Where duplicate analyses were performed, the lower of the two values was used to calculate the results.

As a comparison of the distribution of pesticide residues in Tasmanian wildlife, Figure 3 shows the median values of ΣDDT over the various areas sampled.

The following exploratory analysis of the data was carried out, in order to isolate areas in which pesticide levels could be considered abnormally high. Comparisons were made between pesticide levels in animals of a given species and given area, and all other pesticide occurrences in that species. Authors compared only areas from which five or more animals of a given species were sampled as shown in Table 3. No such comparison was possible in Gawler, Cape Direction, or Preservation Islant (8, 48, and 57 areas, respectively) because the species sampled in these areas were not sampled anywhere else in Tasmania.

Comparisons between five-point summaries can be made by representing them as box and whisker plots (*8*). For example, the five-point summaries of DDE levels in eels from Wesley Vale and eels from all other places

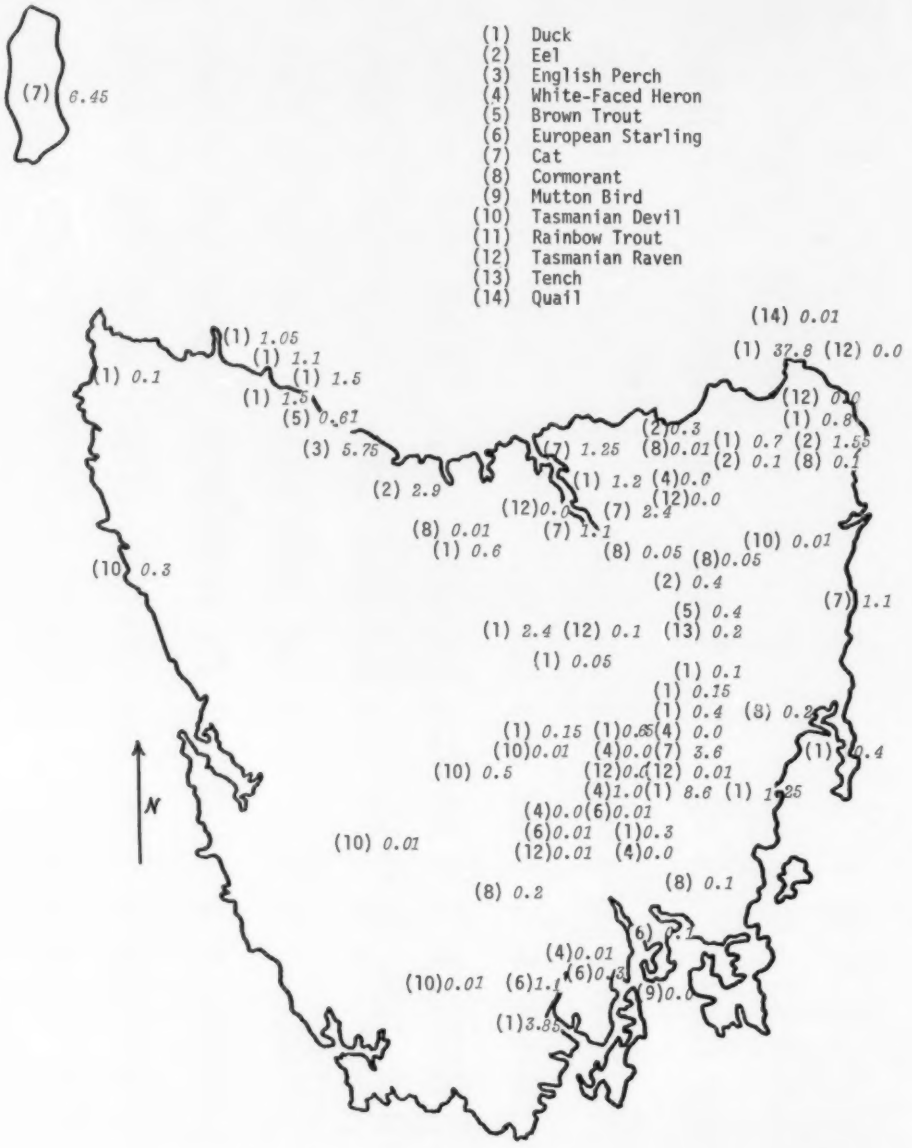

FIGURE 3. *Median values of ΣDDT, ppm, in animals from Tasmania, Australia—1975–77*

TABLE 3. *Areas from which five or more animals of a given species were sampled for organochlorine pesticide residue analyses, Tasmania, Australia—1975–77*

Area [1]	1	3	7	8	9	16	16	17	18	23	24	24	26	26	33
Species [2]	7	1	5	3	2	1	2	2	2	1	5	13	1	12	1
Sample size:															
given area	20	6	23	30	29	9	6	5	15	10	5	12	6	16	26
remaining areas	14	179	5	0	38	176	61	62	52	175	23	0	179	34	159
Area [1]	34	34	34	34	37	39	39	40	41	42	45	48	49	50	57
Species [2]	1	4	7	12	2	1	4	6	6	1	6	9	6	1	14
Sample size:															
given area	37	5	9	23	12	20	5	13	7	19	19	31	30	22	6
remaining areas	148	13	25	27	55	165	13	59	65	166	53	0	42	163	0

[1] See Figure 2 for key.
[2] See Figure 3 for key.

TABLE 4. *DDE levels in eels, Tasmania, Australia—1975–77*

Wesley Vale, Sample Size 29	Other Areas, Sample Size 38
Residue, ppm	
8.2	1.2
1.9	0.5
1.1	0.2
0.8	0.2
0.3	0.0

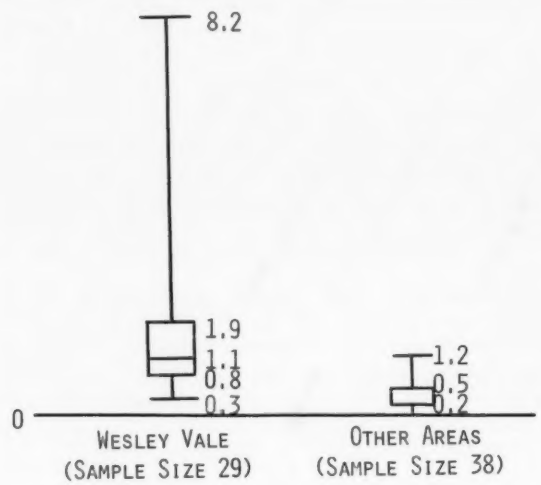

FIGURE 4. *Box and whisker plot of the five-point summaries for ppm DDE in eels, Tasmania, Australia—1975–77*

are given in Table 4; a box and whisker plot for each summary is shown in Figure 4. These are drawn to scale with key readings marked.

It is immediately apparent that DDE levels in eels from Wesley Vale are high compared to those eels from other areas. In fact, about 90 percent of the Wesley Vale readings are above 0.7 ppm, whereas about 84 percent of the remaining readings are below this level. This result is interpreted as a location effect on the DDE levels in eels.

The above analysis was carried out for all of the areas and species listed in Table 3, with the results given in Table 5. The final column in Table 5 lists the pesticides for a location effect of the area on the species shown.

TABLE 5. *Location effects on organochlorine pesticide levels in five species of animals from Tasmania, Australia, 1975–77*

	Area	Species	n^1	n^2	Pesticide
1	(King Island)	cat	20	14	HCB, DDE, TDE, DDT
9	(Wesley Vale)	eel	29	38	DDE, dieldrin, TDE, DDT
26	(Cressy)	Tasmanian raven	16	34	DDE
34	(Ross)	duck	37	148	Dieldrin
49	(Glen Huon)	European starling	30	42	DDE
50	(Huon River)	duck	22	163	DDE, DDT

[1] Number of animals of the given species sampled in the given area.
[2] Number of animals of the given species sampled elsewhere.

A direct comparison of pesticide levels in different species was not as promising because there were very few areas where more than one species was sampled. However, the procedure outlined above was carried out for Big Waterhouse Lagoon, South Esk River, Cressy, Ross, and Lake Sorell (areas 16, 24, 26, 34, and 39, respectively) indicating that feral cats showed high levels of pesticide intake, followed in decreasing order by fish, ducks, and other birds. The results warrant further investigation.

Comparison with Other Studies

A comparison of the present study with similar studies elsewhere (*1, 3, 5, 7, 9,*) shows that neither Tasmania nor Macquarie Island can be regarded as biologically isolated. Highly efficient biological concentration and transportation mechanisms ensure that residues will reach such places from continental areas where relatively larger amounts of pesticides have been used.

Apparently, pesticide residue levels in Tasmanian wildlife are very similar to levels in other parts of the world where fairly strict controls have been implemented for several years. In the Canadian Great Lakes region, persistence and fate of DDT and aldrin/dieldrin in soils, streams, rivers, lakes, and the aquatic food chain has been intensively studied (*5*). It was found, as must be similarly concluded in Tasmania, that DDT and, to a lesser extent, dieldrin contamination is widespread, and that the major sources of contamination are from

recreational and urban uses rather than from agricultural uses of insecticides.

Acknowledgments

Authors thank D. Lynch, Tasmanian Inland Fisheries Commission; I. Eberhard and J. Burgess, Tasmanian National Parks and Wildlife Service; L. Woodhouse, Tasmanian Department of the Environment; E. Martyn and R. Hardy, Tasmanian Department of Agriculture; A. Richardson, Department of Zoology, University of Tasmania; F. Ellis, Victoria Museum; T. P. Speed, University of Western Australia; for helpful discussions on the handling of the data. Authors also thank R. F. Williams, Main Roads Department, Western Australia, for computing the results.

LITERATURE CITED

(*1*) *Bevenue, A. 1976.* The bioconcentration aspects of DDT in the environment. Residue Rev. 61:37–112.

(*2*) *Bowman, M. C., and M. Beroza. 1965.* Extraction *p*-values of pesticides and related compounds in six binary solvent systems. J. Assoc. Off. Agric. Chem. 48 (5):943–952.

(*3*) *Cox, J. L. 1972.* DDT residues in marine phytoplankton. Residue Rev. 44:23–38.

(*4*) *Foster, T. S. 1974.* Physiological and biological effects of pesticide residues in poultry. Residue Rev. 51:69–121.

(*5*) *Harris, C. R., and J. R. W. Miles. 1975.* Pesticide residues in the Great Lakes Region of Canada. Residue Rev. 57:28–79.

(*6*) *Holden, A. V., and K. Marsden. 1969.* Single-stage clean-up of animal tissue extracts for organochlorine residue analysis. J. Chromatogr. 44(1969):481–492.

(*7*) *Spencer, W. F. 1975.* Movement of DDT and its derivatives into the atmosphere. Residue Rev. 59:91–117.

(*8*) Turkey, J. W. *1976.* Exploratory Data Analysis. Addison-Wesley, Boston, Mass.

(*9*) *Ware, G. W. 1975.* Effects of DDT on reproduction in higher animals. Residue Rev. 59:119–140.

DDT in Northern Pike (Esox lucius) *from the Richelieu River, Québec, Canada, 1974–75*

Serge Boileau,[1] M. Baril,[2] and J. G. Alary[1]

ABSTRACT

Concentrations of DDT, TDE, DDE, and ΣDDT were determined in homogenized whole fish samples of 129 northern pike (Esox lucius). *These fish were netted between June 1974 and June 1975 in the first 10 km of the Richelieu River flowing in Canadian territory. Two years after the banning of DDT, ΣDDT levels ranged from 0.2 ppm fresh body weight in two-year-old specimens to 1.5 ppm in a six-year-old pike. Residues increased greatly with age, and significant seasonal variations in the ΣDDT levels were found in five- and six-year-old pike.*

Introduction

Much effort has been devoted to the qualitative and quantitative determination of organochlorine pesticide residues in North American wildlife. Attention has also been given to determining pesticide residues in marine life, i.e., in the New Jersey salt marsh snail (*5*) and in channel catfish in the Des Moines River (*8*).

In the present study, authors relate levels of DDT, TDE, DDE, and ΣDDT in the northern pike (*Esox lucius*), to the period of capture and the age of the specimens. The pike occupies the highest trophic level of the Richelieu River.

The Richelieu River is the outlet of Lake Champlain. The latter is the sixth largest freshwater body in the United States. Hydrologically, Lake Champlain is part of the St. Lawrence Basin. It is both an interstate and an international body of water, with 62 percent of its surface area in Vermont, 35 percent in New York, and 3 percent in Québec, Canada. Draining an 8,234-square-mile basin, through residential, industrial, and agricultural areas (*4*), the lake flows northward and discharges through the Richelieu River.

Sampling

Fortin and Fournier found that, during its lifetime, *Esox lucius* inhabits an area with a radius of approximately two miles (*6*). Therefore, all the specimens were captured in the first 10 km of the river flowing in Canadian territory.

A total of 149 fish were captured by gillnet as follows: 42 between June 1 and August 15, 1974 (period 1); 42 between August 16 and November 15, 1974 (period 2); and 45 between November 16, 1974, and June 1, 1975 (period 3). All fish appeared to be healthy at the time of collection.

Fresh weight was determined immediately. Scales and opercular bones were collected for the estimation of age (*7*), and the fish were wrapped in aluminum foil to prevent desiccation. The error in assigning age to pike is not known but it increases as the age increases. All fish were frozen at —30°C less than three hours after their capture.

Analytical Procedures

Residues were extracted by the method of Porter et al. (*11*) with few modifications. All solvents were pesticide grade quality. The sodium sulfate was conditioned at 650°C for 48 hours and was allowed to cool in an air-tight desiccator.

The Florisil was conditioned at 650°C for 72 hours, partially rehydrated with 2 percent water, and stored in a dark, air-tight glass container.

For each set of analyses, an entire frozen fish was cut into 20 cm^3 pieces. The fish cubes were thawed in 3 ml of 1:1 diethyl ether–petroleum ether/gram initial fresh weight before being homogenized for 3 minutes at 20,000 rpm in a 1-gallon stainless steel Waring blender. The homogenate was centrifuged at 3000 g for 15 minutes. The supernate was dehydrated on a 2.5-cm × 40-cm-long column of anhydrous sodium sulfate. The eluant was collected in a round-bottom flask and evaporated to near dryness in a flash evaporator. The last traces of ether were removed with a stream of nitrogen. and the remaining substance was assumed to be total fat. Five grams of fat was then dissolved in 40 ml of *n*-hexane, and the residue was partitioned between *n*-hexane and 50 ml acetonitrile-saturated *n*-hexane. This extraction was repeated four times.

[1] Department des Sciences Biologiques, Universite du Quebec a Montreal, C.P. 8888, Succ. A, Montreal, Quebec, Canada H3C 3P8.
[2] Department d'Hygiene des Milieux, Universite de Montreal, C.P. 6128, Succ. A, Montreal, Quebec, Canada H3C 3P8.

The 200 ml of acetonitrile–*n*-hexane was collected in a 1-liter decantation flask to which was added 200 ml *n*-hexane, 10 ml dichloromethane, and 50 ml saturated sodium sulfate solution. The mixture was shaken for 2 minutes, 500 ml water was added, and then the mixture was shaken for an additional 2 minutes. The aqueous layer was decanted, the hexane phase was washed with three 150-ml portions of water, and finally dried on a 2.5-cm × 40-cm-long column of anhydrous sodium sulfate. The hexane solution was evaporated to approximately 3 ml. These last 3 ml were eluted through a 2.5-cm × 30-cm-long Florisil column with a mixture of 210 ml *n*-hexane and 90 ml dichloromethane. The column had previously been washed with 150 ml *n*-hexane.

The eluted solution was evaporated to approximately 1 ml, and the final volume was diluted to 10 ml with *n*-hexane.

A sample solution of 1 μl or less was injected into a Tracor Microtek Model 220 gas chromatograph equipped with a ^{63}Ni electron-capture linearizer detector. Instrument parameters and operating conditions follow:

Columns:	silanized borosilicate glass, 4.75 mm ID × 1.80 m long, packed with: (1) a mixture of 2 percent OV-17 and 2 percent OV-210 on 100–120-mesh Gas-Chrom Q (2) a mixture of 1 percent OV-17 and 3 percent OV-210 on 100–120-mesh Gas-Chrom Q
Temperatures:	detector 300°C injector 215°C columns 200°C
Carrier gas:	a mixture of 95 percent argon and 5 percent methane flowing at 70 ml/minute.

The area under the peak was measured with a printing disc integrator and the surface was used to quantitate the residues. Recoveries were 92 percent for DDT, 91 percent for DDE, and 89 percent for TDE. No corrections were made for recovery rates. The method precision has not been accounted for in the statistical treatment of the data.

Confirmatory tests consisted of rerunning the samples, on both columns, after they had been spiked with pure residues.

Lower limits of detection were 0.001 ppm fresh body weight for DDT, TDE, and DDE.

Results

Age of the pike varied from two to six years. Average fresh body weight ranged from 320 to 1700 g and the average percentage of fat varied from 1.1 to 1.9 (Table 1).

One-way variance analysis of the fresh body weight showed the following: Weights of the two-year-old pike were significantly higher ($P<0.05$) during period 3. Weights of three- and four-year-old pike were significantly lower ($P<0.05$) during period 1. Weights of five- and six-year-old specimens did not vary significantly with the period of capture. One-way variance analysis applied to percentage fat showed that the level of fat did not fluctuate with the season of capture; and the two-year-old fish had a significantly lower ($P<0.05$) lipid content that the other age groups, but the lipid contents were not significantly different within the two-year-old group.

Variation due to sex could not be evaluated from these data because of the small number of females.

p,p'-DDT RESIDUES

Table 2 shows the average concentration, standard

TABLE 1. *Fresh body weight and percentage fat, by age group and period of capture, of northern pike* (Esox lucius) *from the Richelieu River, Québec, Canada—1974–75*

Age, Years	Period of Capture[1]	*n*	Fresh Body Weight			Percentage Fat		
			$\bar{x}$	S.D.	Range	$\bar{x}$	S.D.	Range
2	1	12	250	70	120–380	1.1	0.35	0.55–1.7
	2	10	230	40	230–330	0.95	0.35	0.35–1.4
	3	12	420	100	240–630	1.3	0.50	0.50–2.1
	A	34	320	100	120–630	1.1	0.42	0.35–2.1
3	1	10	420	180	180–750	1.6	0.53	0.95–2.9
	2	12	880	100	700–1000	1.5	0.55	0.55–2.4
	3	13	920	160	750–1200	1.6	0.65	0.55–2.9
	A	35	760	260	180–1200	1.6	0.59	0.55–2.9
4	1	10	1100	150	720–1300	2.1	0.88	0.90–3.8
	2	10	1100	140	770–1300	1.4	0.63	0.60–2.9
	3	12	880	200	630–1200	1.5	0.63	0.75–2.7
	A	32	1000	200	630–1300	1.7	0.77	0.60–3.8
5	1	5	1300	280	990–1700	1.9	0.97	0.60–3.3
	2	6	1600	310	1200–2100	1.9	0.85	0.70–3.1
	3	4	1200	190	1000–1500	2.0	1.0	0.80–3.2
	A	15	1400	300	990–2100	1.9	0.87	0.60–3.3
6	1	5	1900	290	1600–2300	2.0	0.84	0.95–3.0
	2	4	1700	220	1500–2000	1.2	0.45	0.80–1.3
	3	4	1600	310	1400–2000	1.7	0.70	0.80–2.3
	A	13	1700	290	1400–2300	1.6	0.73	0.80–3.0

NOTE: A = values for the age group regardless of period of capture.
[1] Period 1: June 1–August 15, 1974; period 2: August 16–November 15, 1974; period 3: November 16, 1974–June 1, 1975.

TABLE 2. p,p'-*DDT residues, by age group and period of capture, in northern pike* (Esox lucius) *from the Richelieu River, Québec, Canada—1974–75*

Age, Years	Period of Capture[2]	*n*	Residues, ppm					
			Wet Weight[1]			Fat		
			$\bar{x}$	S.D.	Range	$\bar{x}$	S.D.	Range
2	1	12	5.4	0.6	4.4–6.5	5.8	2.4	3.1–11
	2	10	6.0	1.0	4.2–7.0	7.5	3.4	3.0–13
	3	12	5.3	1.5	3.1–7.5	4.9	2.8	2.1–9.9
	A	34	5.5	1.1	3.1–7.5	5.9	3.0	2.1–13
3	1	10	12	2.7	7.3–15	7.8	3.5	3.3–14
	2	12	9.5	1.0	8.4–11	7.6	4.0	3.1–18
	3	13	11	1.9	7.8–14	8.9	6.3	2.7–26
	A	35	11	2.1	7.3–15	8.1	4.8	2.7–26
4	1	10	14	2.2	11–17	8.2	4.5	3.2–17
	2	10	11	1.3	8.4–12	9.0	3.2	3.5–14
	3	12	11	2.7	7.7–16	8.9	5.1	3.2–19
	A	32	12	2.5	7.7–17	8.7	4.3	3.2–19
5	1	5	20	4.4	15–26	14	8.7	6.6–28
	2	6	14	2.5	10–17	9.5	6.2	5.5–22
	3	4	21	3.1	17–24	14	9.1	6.1–27
	A	15	18	4.4	10–26	12	7.6	5.5–28
6	1	5	39	5.5	31–46	24	11	10–39
	2	4	21	4.2	17–27	20	8.0	11–30
	3	4	38	3.7	34–42	27	17	16–52
	A	13	33	9.4	17–46	24	12	10–52

NOTE: A = values for the age group regardless of period of capture.
[1] Values multiplied by 100.
[2] Period 1: June 1–August 15, 1974; period 2: August 16–November 15, 1974; period 3: November 16, 1974–June 1, 1975.

deviation, and the range of values of *p,p'*-DDT in ppm wet weight multiplied by 100 and in ppm fat.

When *p,p'*-DDT residues were expressed as ppm wet body weight, one-way variance analysis showed the following: There were no seasonal variations in *p,p'*-DDT levels in the two- and three-year-old fish. *p,p'*-DDT levels in the four-year-old pike caught during period 1 were significantly higher ($P<0.05$) than levels in four-year olds caught during the other two periods. *p,p'*-DDT levels in five- and six-year-old pike caught during period 2 were significantly lower ($P<0.05$) than levels in five- and six-year olds caught during the other two periods. When comparing the age groups, regardless of the period of capture, authors found a significant increase ($P<0.05$) in residue levels with age except between the three- and four-year-old groups.

On the other hand, no seasonal variation could be detected when residues were expressed as ppm fat; the increase of residues with age was significant ($P<0.05$) except between the three- and four-year-old fish and between the four- and five-year-old fish.

p,p'-TDE RESIDUES

Table 3 shows the average concentration, standard deviation, and the range of values of *p,p'*-TDE in ppm wet weight multiplied by 100 and in ppm fat. When the results were expressed as ppm wet body weight, one-way variance analysis showed the following:

There were no seasonal variations in *p,p'*-TDE levels in the two- and three-year-old fish. *p,p'*-TDE levels in four-year-old pike caught during period 2 were significantly lower ($P<0.05$) than levels in four-year-olds caught during the other two periods. *p,p'*-TDE levels in five-year-old pike caught during period 3 were significantly higher ($P<0.05$) than levels in five-year olds caught during the other two periods. *p,p'*-TDE levels in six-year-old pike caught during period 1 were significantly higher ($P<0.05$) than levels in six-year olds caught during period 2. *p,p'*-TDE levels increased significantly ($P<0.05$) between the three- and four-year-old fish and between the four- and five-year-old groups.

When the *p,p'*-TDE residues were expressed as ppm fat, authors found the following:

There were no seasonal variations in *p,p'*-TDE levels in the three-, five-, and six-year-old groups. *p,p'*-TDE levels in two-year-old pike were significantly lower ($P<0.05$) in fish caught during period 1 than levels in two-year olds caught during period 2, *p,p'*-TDE levels in four-year-old pike caught during period 2 were significantly lower ($P<0.05$) than levels in four-year olds caught during period 3, *p,p'*-TDE residue levels increased significantly ($P<0.05$) with age except between the three- and four-year-old groups and between the four- and five-year-old groups.

p,p'-DDE RESIDUES

Table 4 shows the average concentration, standard deviation, and range of values of *p,p'*-DDE as ppm wet weight multiplied by 100 and as ppm fat. When the residues were expressed as ppm wet weight, one-way variance analysis showed the following: There were no seasonal variations in *p,p'*-DDE levels in the 2- and 3-year-old fish. *p,p'*-DDE levels were significantly higher ($P<0.05$) in 4-, 5-, and 6-year-old pike caught during period 1 than levels in 4-, 5-, and 6-year olds

TABLE 3. p,p'-*TDE residues, by age group and period of capture, in northern pike* (Esox lucius) *from the Richelieu River, Quebec, Canada—1974–75*

Age, Years	Period of Capture [2]	*n*	Residues, ppm: Wet Weight [1] $\bar{x}$	S.D.	Range	Fat $\bar{x}$	S.D.	Range
2	1	12	1.8	0.7	1.2–3.3	1.8	1.1	0.9–4.8
	2	10	2.4	0.7	1.0–3.0	3.0	1.3	0.7–5.4
	3	12	3.1	1.0	1.7–4.7	2.8	1.5	0.9–6.3
	A	34	2.4	1.0	1.0–4.7	2.5	1.4	0.7–6.3
3	1	10	4.5	1.4	2.7–6.8	3.0	1.2	1.4–4.4
	2	12	4.8	1.4	2.4–6.9	3.9	2.8	1.0–12
	3	13	6.9	2.4	3.7–11	5.5	4.1	1.5–16
	A	35	5.5	2.1	2.4–11	4.2	3.1	1.0–16
4	1	10	7.8	1.6	5.9–11	4.4	2.1	2.4–9.0
	2	10	4.1	1.4	1.8–6.1	3.4	1.3	1.7–5.8
	3	12	8.6	2.2	5.4–12	7.1	4.4	2.0–15
	A	32	6.9	2.6	1.8–12	5.1	3.4	1.7–15
5	1	5	9.4	1.8	8.6–12	6.7	4.7	3.6–15
	2	6	7.3	2.0	5.2–11	4.6	2.7	3.2–10
	3	4	13	2.6	10–16	8.2	4.0	4.4–13
	A	15	9.5	3.1	5.2–16	6.3	3.8	3.2–15
6	1	5	18	2.8	15–21	11	4.7	5.2–16
	2	4	12	3.5	7.7–16	12	4.9	4.3–15
	3	4	21	7.7	12–31	15	9.3	9.1–28
	A	13	17	5.9	7.7–31	12	6.1	4.3–28

NOTE: A = values for the age group regardless of period of capture.
[1] Values multiplied by 100.
[2] Period 1: June 1–August 15, 1974; period 2: August 16–November 15, 1974; period 3: November 16, 1974–June 1, 1975.

TABLE 4. p,p'-*DDE residues, by age group and period of capture, in northern pike* (Esox lucius) *from the Richelieu River, Quebec, Canada—1974–75*

Age, Years	Period of Capture [2]	*n*	Residues, ppm: Wet Weight [1] $\bar{x}$	S.D.	Range	Fat $\bar{x}$	S.D.	Range
2	1	12	11	1.3	10–15	12	3.9	7.0–19
	2	10	12	1.3	9.0–13	15	8.9	8.7–35
	3	12	11	1.1	9.0–14	10	6.7	4.1–27
	A	34	11	1.5	9.0–15	12	6.7	4.1–35
3	1	10	21	4.3	16–27	14	6.4	5.7–28
	2	12	22	2.0	16–26	17	10	9.1–43
	3	13	18	1.6	16–20	14	6.6	5.7–29
	A	35	20	3.5	16–27	15	7.9	5.7–43
4	1	10	32	4.9	25–39	19	9.7	9.1–40
	2	10	24	3.1	18–27	21	11	7.8–46
	3	12	26	2.6	22–29	20	7.9	9.7–32
	A	32	27	4.7	18–39	20	9.2	7.8–46
5	1	5	69	3.8	62–72	51	40	19–120
	2	6	36	6.2	29–44	24	13	10–44
	3	4	37	4.2	33–41	26	18	11–51
	A	15	47	16	29–72	33	27	10–120
6	1	5	130	12	110–140	80	44	46–150
	2	4	44	4.2	39–48	41	15	27–58
	3	4	60	6.0	66–54	42	21	29–71
	A	13	81	40	39–140	56	35	27–150

NOTE: A = values for the age group regardless of period of capture.
[1] Values multiplied by 100.
[2] Period 1: June 1–August 15, 1974; period 2: August 16–November 15, 1974; period 3: November 16, 1974–June 1, 1975.

caught during periods 2 and 3. *p,p'*-DDE levels increased significantly ($P<0.05$) with age.

When the residues were expressed as ppm fat, authors found that there were no seasonal variations in *p,p'*-DDE levels in the 2-, 3-, and 4-year-old pike. *p,p'*-DDE levels in the 5- and 6-year-old pike caught during period 1 were significantly higher ($P<0.05$) than levels in 5- and 6-year olds caught during the other two periods. *p,p'*-DDE levels increased significantly ($P<0.05$) with age except between the 2- and 3-year-old groups.

ΣDDT RESIDUES

Table 5 shows average concentration, standard deviation, and range of values for ΣDDT as ppm wet weight multiplied by 100 and as ppm fat. When residues were expressed as ppm wet weight, one-way variance analysis showed the following: There were no seasonal variations in ΣDDT residues in the two- and three-year-old fish; ΣDDT levels in four-, five-, and six-year-old pike were significantly lower ($P<0.05$) during period 2 and significantly higher ($P<0.05$) during period 1 than levels in four-, five-, and six-year olds caught during the other two periods (Fig. 1). ΣDDT levels increased significantly ($P<0.01$) with age (Fig. 2).

When ΣDDT residues were expressed as ppm fat, authors found there were no significant seasonal variations in the ΣDDT levels (Fig. 3); and ΣDDT levels increased significantly ($P<0.05$) with age (Fig. 4).

The water level of Lake Champlain, recorded at Rouses Point between June 1974 and June 1975, is illustrated in Figure 5 as the mean, maximum, and minimum for each month.

TABLE 5. *ΣDDT residue, by age group and period of capture, in northern pike* (Esox lucius) *from the Richelieu River, Quebec, Canada—1974–75*

Age, Years	Period of Capture [2]	n	Residues, ppm: Wet Weight [1] $\bar{x}$	S.D.	Range	Fat $\bar{x}$	S.D.	Range
2	1	12	19	1	16–22	20	7	11–33
	2	10	20	1	18–22	25	12	13–52
	3	12	20	3	14–26	18	10	10–34
	A	34	19	2	14–26	19	11	10–52
3	1	10	37	4	32–43	19	14	11–45
	2	12	36	3	32–40	29	16	15–72
	3	13	36	4	29–41	28	16	10–58
	A	35	36	3	29–43	26	14	10–72
4	1	10	53	4	48–60	31	16	15–63
	2	10	39	3	33–43	33	14	13–63
	3	12	46	2	42–48	36	16	16–64
	A	32	46	7	33–60	34	15	13–64
5	1	5	98	4	93–100	71	51	29–160
	2	6	57	4	54–62	38	21	19–76
	3	4	71	3	67–74	47	31	21–91
	A	15	74	18	54–100	50	38	19–160
6	1	5	190	8	170–190	110	57	61–200
	2	4	77	4	75–82	87	17	61–100
	3	4	120	4	110–120	83	46	53–150
	A	13	130	48	75–190	96	43	53–200

NOTE: A = values for the age group regardless of period of capture.
[1] Values multiplied by 100.
[2] Period 1: June 1–August 15, 1974; period 2: August 16–November 15, 1974; period 3: November 16, 1974–June 1, 1975.

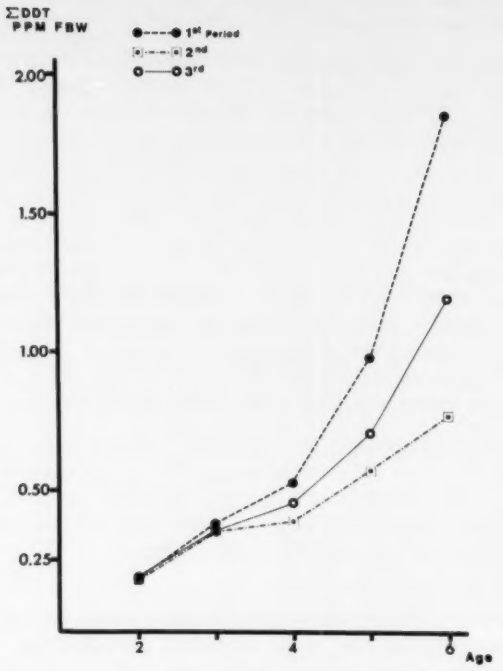

FIGURE 1. *Average ΣDDT levels, ppm wet weight, in five age groups of northern pike* (Esox lucius) *during three periods of capture, Richelieu River, Québec, Canada—1974–75*

Discussion

Buhler et al. (*1, 2*) reported that whole-body DDT residues increased with size for salmon. This correlates well with the present data showing that residues increased significantly with age of the northern pike. The conclusion is even more explicit when results are expressed on a fresh-body-weight basis compared to a lipid basis (Fig. 2 versus Fig. 4).

The extent to which DDT residues affected the physiology of pike was not determined, but authors feel that a human population whose diet was based on this fish would certainly be exposed to large amounts of residues.

Seasonal variations in residue levels in fish have received little attention. Kelso et al. (*9*) working with six different species, found that residue levels peaked in November and were at a minimum during May and July; these variations corresponded to the seasonal domestic and agricultural use of pesticides in the watershed.

Simpson et al. (*12*) surveyed mercury content in food and fish, including a wide range of freshwater fish. In specimens collected from Pickwick Reservoir in Tennes-

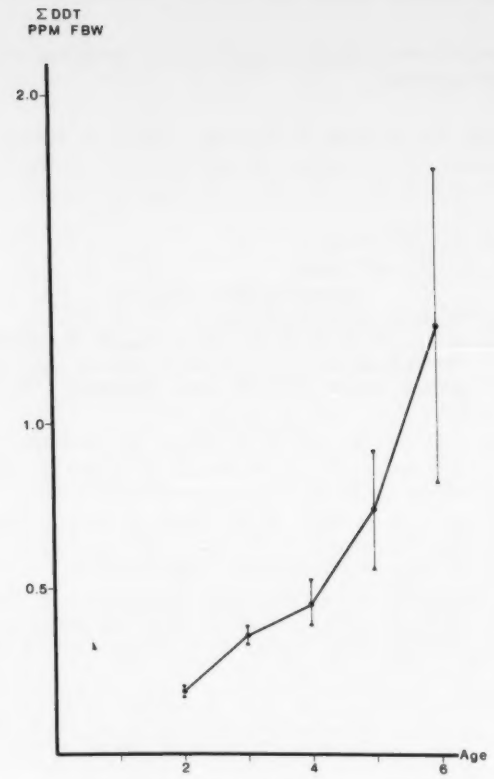

FIGURE 2. *Average ΣDDT and standard deviation, ppm wet weight, for five age groups of northern pike* (Esox *lucius*) *from the Richelieu River, Québec, Canada—1974–75*

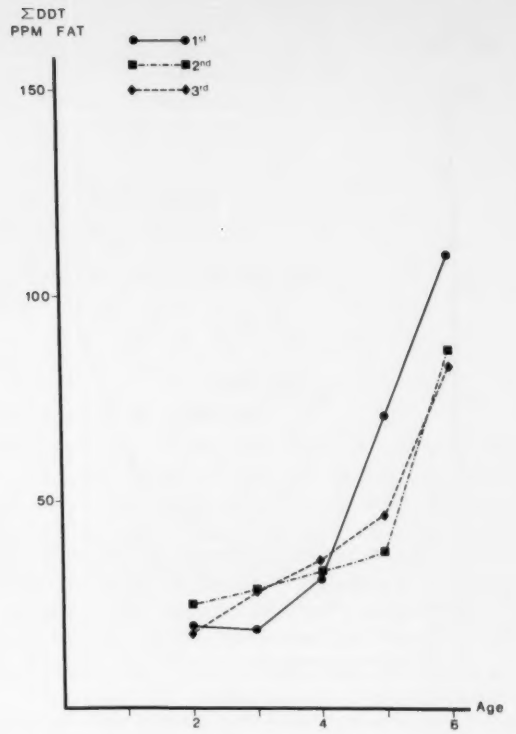

FIGURE 3. *Average ΣDDT levels, ppm fat, in five age groups of northern pike* (Esox lucius) *during three periods of capture, Richelieu River, Québec, Canada—1974–75*

see, they found maximum mercury concentrations between June and September 1970 and between April and July 1971.

In a study of oysters from the Caloosahatchee River drainage basin in Florida, Butler (*3*) observed that the seasonal fluctuation of pesticide residues indicated an agricultural or at least a scheduled use of DDT. He found it significant that extensive acreage in this drainage basin was devoted to the culture of sugarcane and sweetcorn crops which would be maturing and receiving fairly heavy pesticide applications during the peak residue periods.

Kellogg and Bulkley (*8*) found a seasonal variation in dieldrin concentrations in the muscle tissue of channel catfish (*Ictalurus punctatus*) that were 300–399-mm long. Three peaks were found, in April, July, and September.

In the present study, a significant seasonal variation of ΣDDT occurred in the older fish groups where results are expressed as ppm fresh body weight, but this variation is not significant when the data are expressed as ppm fat. It was also impossible to detect a significant seasonal variation of lipid levels in these pike.

The seasonal variation in the present results could hardly be attributed to the agricultural use of DDT because the pesticide was banned in 1973.

Therefore, authors must hypothesize that there is a persistent input of DDT that contaminates the prey of pike. According to Woodwell et al. (*13*), although DDT has been banned in Canada and the United States, the aerial movement of DDT worldwide could account for a great deal of DDT input to aquatic fauna.

Fischer et al. (*4*) reported that the drainage basin of Lake Champlain includes 10,540 acres of apple orchards: 5,740 acres in New York and 4,800 acres in Vermont. Kuhr et al. (*10*) found up to 357 ppm DDT in the first six inches of soil in orchards that had not been sprayed with DDT for more than 15 years. Over 70 percent of the aged deposits were still in the form of unchanged DDT, the remainder being the metabolites DDE and TDE.

Authors can only speculate that rainfall is the major cause of DDT input to the aquatic system of Lake Champlain. Figure 5 shows that the lower water levels correspond to the second period of capture when minimum residues were found. One would expect a greater

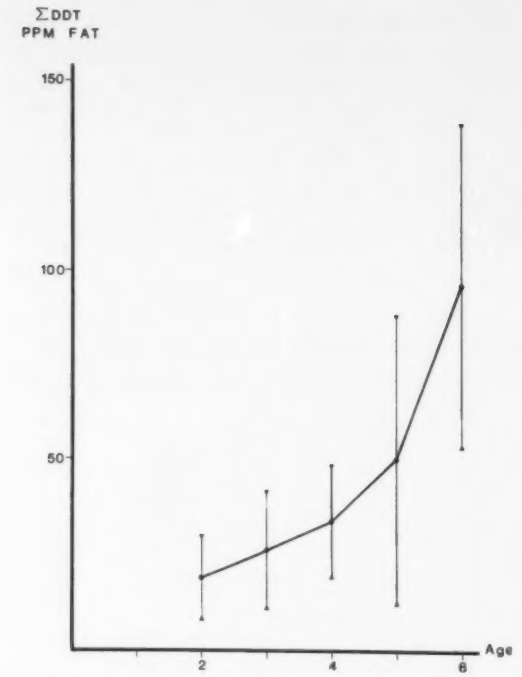

FIGURE 4. *Average ΣDDT and standard deviation, ppm fat, for five age groups of northern pike* (Esox lucius) *from the Richelieu River, Québec, Canada—1974–75*

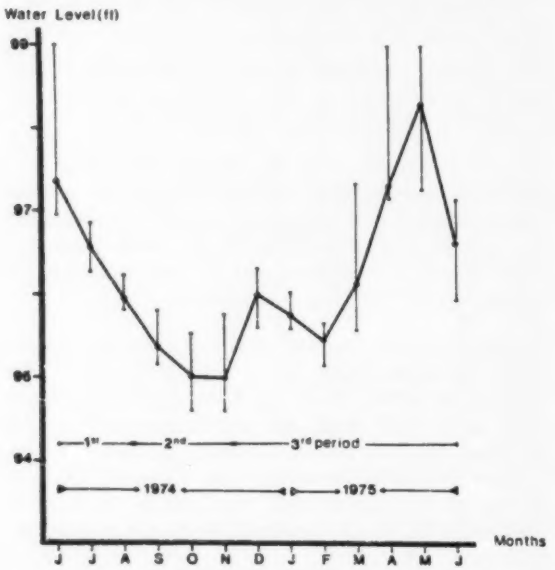

FIGURE 5. *Monthly mean, maximum, and minimum water levels of Lake Champlain recorded at Rouses Point, between June 1974 and June 1975*

lapse of time between minimum water levels and minimum residues.

More data on water analysis are needed to determine whether rainfall deposits the airborne DDT or whether it leaches residues present in the upper soil layers.

LITERATURE CITED

(1) *Buhler, D. R., M. E. Rasmusson, and W. E. Shanks. 1969.* Chronic oral DDT toxicity in juvenile coho and chinook salmon. Toxicol. Appl. Pharmacol. 14(3): 535–555.

(2) *Buhler, D. R., and W. E. Shanks. 1970.* Influence of body weight on chronic oral DDT toxicity in coho salmon. J. Fish. Res. Board Can. 27(2):347–358.

(3) *Butler, P. A. 1973.* Organochlorine residues in estuarine mollusks, 1965–72, National Pesticide Monitoring Program. Pestic. Monit. J. 6(4):238–362.

(4) *Fischer, R. M., M. Zeller, and T. L. Davis. 1976.* Lake Champlain planning guide for water and related land resources. New England River Basins Commission, Boston, Mass. 12 pp.

(5) *Fitzpatrick, G., and D. J. Sutherland. 1976.* Uptake of the mosquito larvicide Temefos by the salt marsh snail, New Jersey, 1973–74. Pestic. Monit. J. 10(1): 4–6.

(6) *Fournier, H. 1979.* M.Sc. Thesis. Université du Québec á Montréal. 32 pp.

(7) *Frost, W., and C. Kipling. 1958.* The determination of the age and growth of pike (*Esox lucius*) from scales and opercular bones. J. Cons. Perm. l'Explor. Mer. 24(1):314–341.

(8) *Kellogg, R. L., and R. V. Bulkley. 1976.* Seasonal concentrations of dieldrin in water, channel catfish, and catfish-food organisms, Des Moines River, Iowa—1971–73. Pestic. Monit. J. 9(4):186–194.

(9) *Kelso, J. R. M., H. R. Mac Crimmon, and D. J. Ecobichon. 1970.* Seasonal insecticide residue changes in tissues of fish from the Grand River, Ontario. Trans. Am. Fish. Soc. 99(2):423–426.

(10) *Kuhr, R. J., A. C. Davis, and J. B. Bourke. 1977.* N. Y. Food Life Sci. 10(3):18–20.

(11) *Porter, M. L., S. J. V. Young, and J. A. Burke. 1970.* A method for the analysis of fish, animal, and poultry tissue for chlorinated pesticide residues. J. Assoc. Off. Anal. Chem. 53(6):1300–1303.

(12) *Simpson, R. E., W. Horwitz, and C. A. Roy. 1974.* Surveys of mercury levels in fish and other foods. Pestic. Monit. J. 7(3/4):127–138.

(13) *Woodwell, G. M., P. P. Craig, and H. A. Johnson. 1971.* DDT in the biosphere: where does it go? Science 174(4014):1101–1107.

Organochlorine Residues in Young Herons from the Upper Mississippi River—1976

Harry M. Ohlendorf,[1] James B. Elder,[2] Rey C. Stendell,[1,3] Gary L. Hensler,[1] and Richard W. Johnson[4]

ABSTRACT

Chicks of great blue herons (Ardea herodias) *from four heronries located near South St. Paul, Royalton, and Wabasha, Minnesota, and La Crosse, Wisconsin, were analyzed for organochlorines. Highest mean wet-weight concentrations, 6.43 ppm PCBs, 1.31 ppm DDE, and 1.90 ppm ΣDDT, were found in the South St. Paul chicks. Among chicks from the other three heronries, most levels were similar, but were significantly lower than levels in South St. Paul chicks. Lowest mean organochlorine levels, 0.37 ppm DDE, 0.38 ppm ΣDDT, and 0.22 ppm PCBs, were found in chicks from Royalton. All birds from South St. Paul and La Crosse contained residues of DDT and TDE whereas only one of the 10 birds from Royalton contained DDT and one contained TDE residues. Five of the 12 birds from Wabasha contained DDT; eight contained TDE. Except for PCB residues in La Crosse heron chicks, the rate of organochlorine residue accumulation in the birds was generally less than the rate of dilution caused by growth.*

Introduction

Residues of toxic chemicals in biological materials are useful for determining the spatial distribution of environmental contamination and for identifying sources of pollution. Mayflies (*Hexagenia bilineata*), for example, were used to determine geographic distribution of residues of polychlorinated biphenyls (PCBs) in the upper Mississippi River (*5*), following the discovery of elevated levels in fish collected from certain segments of the river (*3, 4, 6*). Similarly, residues in heron eggs indicated geographic and species differences in concentrations of organochlorine pesticides and PCBs (*7–10*). In the present study, authors collected great blue heron (*Ardea herodias*) chicks at four locations along the upper Mississippi River to determine geographic variation in selected organochlorine residues.

Methods

COLLECTION AND DISSECTION

Great blue heron chicks were collected June 2–8, 1976, at the following sites: 5 km west of Royalton, Minnesota; Pig's Eye Island, near South St. Paul, Minnesota; Upper Mississippi River Wild Life and Fish Refuge, near Wabasha, Minnesota; and Upper Mississippi River Wild Life and Fish Refuge, 3 km south of La Crosse, Wisconsin (Fig. 1). The birds were collected as near to fledging as possible, but before they were able to fly.

One young heron with a broken wing was found alive and alert on the ground in the Wabasha heronry. Although the bird was analyzed and included in Table 1, it was not included in comparisons of localities or nests because authors determined from its thin body

FIGURE 1. *Upper Mississippi River in Minnesota and Wisconsin, showing cities near which young great blue herons were collected in 1976*

[1] Patuxent Wildlife Research Center, Fish and Wildlife Service, U.S. Department of the Interior, Laurel, Md. 20811.

[2] Fish and Wildlife Service, U.S. Department of the Interior, Twin Cities, Minn. 55111.

[3] Present address: Fish and Wildlife Service, U.S. Department of the Interior, Washington, D.C. 20240.

[4] Raltech Scientific Services, Inc. (formerly WARF Institute, Inc.), P.O. Box 7545, Madison, Wis. 53707.

TABLE 1. *Mean weight, percent lipid, and organochlorine residues in great blue herons, upper Mississippi River, 1976*[1]

Nest Number (Number of Birds)	Body Weight, g	Carcass Weight, g	Lipid Content, %	Residues, ppm Wet Weight			Residues, ppm Lipid Weight		
				DDE	ΣDDT	PCBs	DDE	ΣDDT	PCBs
ROYALTON, MINN.; 10 SPECIMENS FROM 4 NESTS									
1 (2)	1120.5	525.0	5.2	0.80	0.80	0.32	15.4	15.4	6.1
2 (1)	544.0	230.0	3.4	0.70	0.70	0.34	20.6	20.6	10.0
3 (4)	1290.5	583.5	3.2	0.22	0.23	0.21	8.5	9.0	7.3
4 (3)	1589.8	753.7	5.1	0.19	0.19	0.15	4.0	4.0	3.1
Locality mean[2]	1271.6 A	587.5 B	4.2 B	0.37 B	0.38 B	0.22 C	9.7 A	9.9 B	6.1 B
SOUTH ST. PAUL, MINN.; 10 SPECIMENS FROM 4 NESTS									
5 (3)	1481.2	752.7	6.5	1.33	1.92	7.21	20.1	28.9	109.8
6 (2)	1810.6	961.0	10.0	1.62	2.31	5.56	16.1	23.0	55.3
7 (2)	2032.5	1064.0	7.1	1.21	1.78	3.54	17.2	25.5	51.0
8 (3)	1991.7	1086.0	9.3	1.16	1.69	8.14	12.5	18.2	87.5
Locality mean[2]	1810.5 A	956.6 A	8.2 A	1.31 A	1.90 A	6.43 A	16.5 A	23.9 A	80.4 A
WABASHA, MINN.; 11 SPECIMENS FROM 5 NESTS									
– (1)[3]	955.0	462.0	0.9	0.50	0.58	2.26	55.6	64.6	251.1
9 (3)	1732.8	793.7	5.5	0.45	0.50	1.86	8.5	9.4	35.7
10 (2)	1551.8	761.5	3.2	0.60	0.75	3.40	19.4	24.1	103.7
11 (2)	1953.2	978.0	6.4	0.20	0.24	1.06	3.3	3.7	16.2
12 (3)	1691.8	867.3	4.5	0.23	0.27	1.53	5.5	6.4	34.6
13 (1)	1157.0	533.0	3.2	0.36	0.42	3.54	11.2	13.0	110.6
Locality mean[4]	1676.5 A	817.7 AB	4.8 B	0.37 B	0.43 B	2.05 BC	9.0 A	10.5 B	51.0 AB
LA CROSSE, WIS.; 11 SPECIMENS FROM 5 NESTS									
14 (1)	2009.0	940.0	6.7	0.34	0.45	1.72	5.1	6.7	25.7
15 (2)	1649.5	819.5	4.8	0.43	0.53	1.84	8.7	10.7	38.4
16 (3)	1783.0	913.3	4.9	0.69	0.84	5.46	13.9	16.8	110.1
17 (3)	1017.2	420.3	3.4	0.81	0.88	0.98	27.0	28.8	31.5
18 (2)	776.5	322.0	3.8	0.52	0.61	2.52	19.1	21.9	96.4
Locality mean[2]	1387.4 A	656.7 B	4.5 B	0.61 B	0.71 B	2.71 B	16.7 A	19.0 AB	65.4 A

[1] Locality means that do not share the same letters are significantly different ($P < 0.05$) from each other (Duncan's Multiple Range Test).
[2] Locality means based on weighted nest means.
[3] This chick was found on the ground with a broken wing and was excluded from all statistical comparisons (see Methods).
[4] Locality mean based on weighted nest means, but excludes first bird listed for this locality.

and low lipid content that it was starving. Another heron that was found on the ground in the Wabasha heronry (Table 1, nest 13) was included as a separate nest because the bird apparently had fallen while collectors were in the colony, although its fall was not observed. Weight, lipid content, and organochlorine residues in this bird were generally similar to those in herons from nest 10. However, the fallen bird was found under a different tree than that containing nest 10, and DDT was not detected in this bird whereas DDT was found in both young from nest 10.

The birds were frozen after collection. Whole body weights were determined before feet, beaks, wing tips, skin, and gastrointestinal tracts were removed; carcasses were then weighed, ground, and frozen until analysis.

ANALYTICAL PROCEDURES

Herons were analyzed for PCBs, DDE, TDE, and DDT by WARF Institute, Inc. (now Raltech Scientific Services, Inc.), Madison, Wisconsin. The individual carcasses were ground and mixed well before subsampling; then a 20-g subsample of each was mixed with about 100 g anhydrous sodium sulfate, covered with aluminum foil, and dried in a hood. The sample was extracted with 50 ml ethyl ether in 50 ml petroleum ether for 10 hours in a Soxhlet extractor.

A 10-ml aliquot of the extract was eluted twice through a column of previously standardized Florisil, first with 150 ml of 5 percent ethyl ether in petroleum ether and next with 250 ml of 15 percent ethyl ether in petroleum ether. The second elution was injected into a gas chromatograph and quantitated for insecticides. The first elution was separated into three fractions by passage through a silica CC–4 column. The first fraction, eluted with 200 ml petroleum ether, contained some late-eluting PCBs. The second fraction, eluted with 400 ml petroleum ether, contained PCBs and small amounts of DDE. The third fraction, eluted with a mixture of 2 ml acetronitrile, 38 ml hexane, and 160 ml methylene chloride, contained DDE, TDE, and DDT. Each fraction was injected into a gas chromatograph for quantitation.

Samples were analyzed on a Hewlett-Packard Model 5710 A gas chromatograph equipped with a linearized Ni^{63} electron-capture detector and an automatic injector. Instrument and operating conditions follow:

Column:	glass, 122 cm long × 4 mm ID, packed with a mixture of 1.5 percent SP-2250 and 1.95 percent SP-2401 on a 100–120-mesh Supelcoport
Temperatures:	column 213°C injector 250°C detector 300°C
Carrier gas:	95 percent argon and 5 percent methane flowing at 45 ml/minute

Residues in 12 samples were confirmed by gas chromatography-mass spectrometry.

A Hewlett-Packard Model 3352 C data system was used for quantitation. PCBs were calculated against Aroclor 1254 on the basis of all peaks except the one with a retention time near DDE. Lower limits of detection were 0.005 ppm for DDE, TDE, and DDT, and 0.01 ppm for PCBs.

Lipid percentages were determined on 5-ml subsamples of the Soxhlet extract.

STATISTICAL PROCEDURES

Authors ran a nested analysis of variance—mixed model (*12*, pp. 248, 261) for weight, lipid content, and each chemical; collection locations were fixed effects and nests within locations were random effects. When authors found statistically significant differences among the locations, they used Duncan's multiple range test to separate locations. In addition, correlation coefficients and linear regressions were calculated for pairs of variables. Statistical Analysis System (SAS) procedures were used to perform the analyses (*1*). Locality means reported in Table 1 are weighted averages of nest means; each nest mean is weighted by the number of chicks from that nest. The level of significance is accepted as $P \leq 0.05$ unless otherwise indicated.

Results

Mean whole body weights of herons from the four localities were not significantly different, but the mean carcass weight of the birds from South St. Paul was significantly greater than means for Royalton or La Crosse birds (Table 1). Mean carcass weight of the birds from Wabasha was not significantly different from that of birds from the other three localities. Carcass weights of the birds averaged 46.2–48.7 percent of their whole body weights at each locality except South St. Paul, where carcasses averaged 52.8 percent of the body weight.

Mean lipid content in the herons from South St. Paul was significantly higher than in birds from the other localities.

Residue data are presented here on a wet-weight basis, but lipid-weight concentrations also are listed in Table 1. Mean concentrations of PCBs, DDE, and ΣDDT in chicks from South St. Paul were significantly greater than in chicks from all other localities, and the PCB mean for La Crosse chicks was higher than that for Royalton chicks. However, the mean PCB concentration in herons from Wabasha was not significantly different from mean concentrations in birds from La Crosse and Royalton. There were no differences in concentrations of DDE or of ΣDDT among the birds from Royalton, Wabasha, and La Crosse.

Residues of DDT *per se* were detected in all herons from La Crosse and South St. Paul, but in only one of the 10 birds from Royalton (Table 1). Highest wet-weight concentration of DDT was 0.1 ppm in a South St. Paul heron. DDT also was detected in five of 12 herons from Wabashha; two were from nest 10 and three were from nest 12. TDE was found in all herons from South St. Paul at levels up to 0.72 ppm, in all from La Crosse; in eight of 12 from Wabasha, and in one of the 10 from Royalton.

When the 42 birds were considered individually, lipid content correlated significantly with carcass weight ($R^2 = 0.48$; $P < 0.0001$); heavier birds had a higher percentage of lipids in their bodies. However, the regression of lipid content against carcass weight (Table 2, Fig. 2) for the birds from South St. Paul was significantly different from that of the birds from the other three localities which did not differ from each other. This relationship further demonstrates the significant differences in carcass weights and lipid contents of birds from the four localities.

Because of the significant differences in residue concentrations among localities (Table 1), authors tested the relationship between wet-weight residue concentrations and carcass weights separately for each locality. Except for PCBs in La Crosse herons, the regression slope was negative; residue concentrations for each chemical at each locality tended to decrease as the birds increased in weight. However, the regression slope was not statistically significant at the $P = 0.05$ level (Table 2, Fig. 3). The negative regression slope of

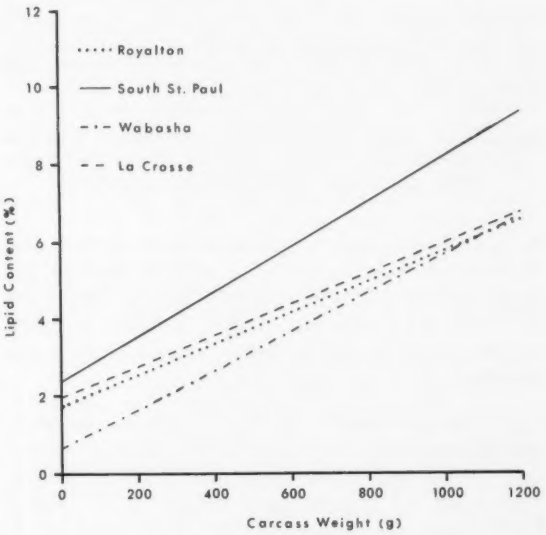

FIGURE 2. *Regression of lipid content against carcass weight in young great blue herons from the upper Mississippi River—1976. See Table 2 for regression equations.*

TABLE 2. *Regression of lipid content and residue concentrations against carcass weight in great blue herons from four upper Mississippi River localities—1976*

Location (Number of Birds)	Lipid Content, %	Residues, ppm Wet Weight		
		DDE	ΣDDT	PCBs
Royalton, Minn. (N = 10; 4 nests)	$Y = 1.76 + 0.004X$	$Y = 0.68 - 0.0005X$	$Y = 0.67 - 0.0005X$	$Y = 0.27 - 0.00007X$
South St. Paul, Minn. (N = 10; 4 nests)	$Y = 2.18 + 0.006X$	$Y = 1.65 - 0.0004X$	$Y = 2.40 - 0.0005X$	$Y = 8.74 - 0.002X$
Wabasha, Minn. (N = 11; 5 nests)	$Y = 0.68 + 0.005X$	$Y = 0.76 - 0.0005X$	$Y = 0.90 - 0.0006X$	$Y = 5.40 - 0.004X$ [1]
La Crosse, Wis. (N = 11; 5 nests)	$Y = 1.99 + 0.004X$ [2]	$Y = 0.76 - 0.0002X$ [2]	$Y = 0.79 - 0.0001X$ [2]	$Y = 0.47 + 0.003X$ [2]
(N = 10; 5 nests)	$Y = 2.44 + 0.003X$	$Y = 0.84 - 0.0003X$	$Y = 0.85 - 0.0002X$	$Y = -1.29 + 0.006X$ [3,4]

[1] Significant at $P = 0.08$.
[2] Regression equation when one of the two young in nest 18 that apparently was starving is omitted from the analysis.
[3] Significant at $P = 0.12$.
[4] Significant at $P = 0.05$.

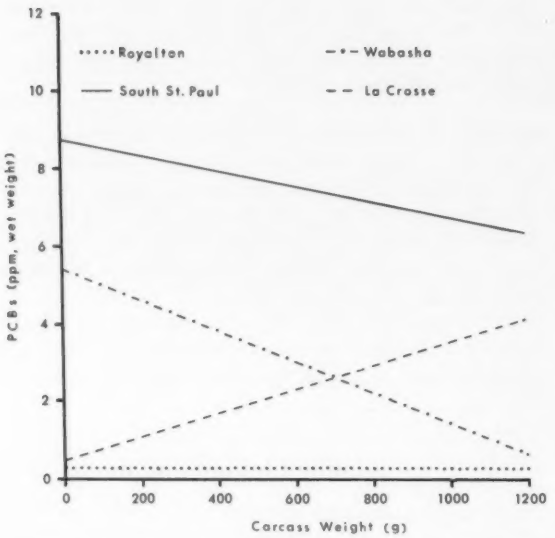

FIGURE 3. *Regression of PCBs against carcass weight in young great blue herons from the upper Mississippi River—1976. See Table 2 for regression equations.*

PCBs against carcass weight for birds from Wabasha, however, was significant at $P = 0.08$. In contrast, the regression slope of PCBs against carcass weight for birds from La Crosse was positive. Residues increased as body weight increased, and the regression slope was significant at $P = 0.12$.

One of the two birds in nest 18, La Crosse, apparently was starving. Its 418 g body weight and 2.0 percent lipid content were much lower than the 1135 g body weight and 5.7 percent lipid content of its sibling. Furthermore, the residue concentrations were much higher in the smaller bird. When the smaller bird was omitted from the analysis, the regression slope for PCBs at La Crosse was significantly positive.

Discussion and Conclusions

Heron chicks from the Royalton nesting colony upstream from the Minneapolis-St. Paul metropolitan area contained the lowest PCB burdens, suggesting that the chicks were being fed prey containing significantly lower residue levels than prey in heronries below the metropolitan area. Authors found the highest organochlorine residue levels in herons from colonies near South St. Paul and La Crosse; residue levels tended to be lower, although the differences were not statistically significant, in herons from the more rural area at Wabasha than in herons from La Crosse. The major sources of PCBs are associated with the Minneapolis-St. Paul and La Crosse metropolitan areas (*3, 4, 6*). ΣDDT residues in the birds may have resulted from the past spraying of DDT for control of Dutch elm disease in Minneapolis-St. Paul and in La Crosse.

Because of reported high residue levels in fish from Lake Pepin (*3, 4, 6*), authors expected PCB residues in herons from Wabasha to be higher than in the birds from South St. Paul. However, herons nesting in the Wabasha colony, which is downstream from Lake Pepin, apparently feed on cleaner prey than do birds from South St. Paul. Most birds from the Wabasha colony probably do not feed in Lake Pepin during the nesting season because the downstream portion of the lake does not provide many favorable shallow-water feeding sites near the colony. Furthermore, there apparently are differences in contamination levels within Lake Pepin; PCB residues are higher at the upper end of the lake than they are at the lower end (*6*).

The negative regression of PCBs against carcass weight of chicks from the Wabasha heronry was significant at $P = 0.08$. This indicates that herons nesting in the colony feed more extensively in Lake Pepin before and after the nesting season than they do while they are feeding their chicks. Great blue herons do not occupy their breeding areas immediately after spring migration, and they disperse soon after the young can fly (*11*, p. 396). The young herons at Wabasha, therefore, may have received higher concentrations of PCBs in the egg, but the residues were being diluted by growth at

a greater rate than were residues in birds at other localities.

Although there was no statistically significant difference in whole body weights of birds from the four locations, the herons from South St. Paul were heavier after dissection, i.e., a smaller proportion of their weight was removed. The significant difference in carcass weights was partly due to the greater amount of lipids in the South St. Paul birds, which indicates that the birds were somewhat older than those from the other localities. Heavy deposition of fat, and hence, increased weight, is typical of late pre-fledging development (*13*, p. 337). If the chicks from South St. Paul were older, they would have had more time to accumulate residues, and because they were also fatter they would have accumulated more residues from the same intake as chicks at other localities.

When comparing residue levels in animals from different geographic areas, it is important to determine whether the lipid content in samples from the various localities is the same. If residue concentrations are not presented on both wet-weight and a lipid-weight basis, the percentage lipid in the samples should be given to allow readers to make the appropriate conversions.

At the beginning of the present study, authors assumed that residues acquired within the egg from the female would have been diluted by growth and that most of the contaminant burden in the heron chicks was acquired through the local food supply. If, for example, a 70-g heron egg contained 1000 μg (14.3 ppm) of contaminant, the chick would have only 1 ppm when it reached 1000 g, owing to dilution alone. Residues in chicks then would indicate local differences in contaminant occurrence along the river.

Organochlorine residues decreased in ducklings as the birds increased in weight (*2*). Those residues were probably transferred through the egg by the parent bird, because no residues were detected in the ducklings' food.

PCB residues were positively correlated with the weight of young herons at La Crosse, undoubtedly reflecting elevated PCB levels in local food sources. Residues increased significantly as the birds grew. At the other three localities, however, the trend was toward lower residues of all chemicals as the birds increased in weight. At these localities the rate of residue accumulation, therefore, was less than the rate of dilution caused by growth.

Authors conclude that there are differences among the four localities, and that the residue levels in birds collected upstream from the metropolitan areas were significantly lower than those affected by pollution downstream. Authors also conclude that birds nesting in the Wabasha Colony were not feeding on the heavily contaminated fish in Lake Pepin during the nesting season.

Acknowledgments

K. Butts, S. Cornelius, D. L. Peterson, and J. L. Smith collected the young herons, and J. P. Hughes dissected them. The Nature Conservancy granted permission for collections at the Royalton site. The Environmental Chemistry Project at the Patuxent Wildlife Research Center analyzed cross-check samples. Authors appreciate reviews and helpful suggestions by T. W. Custer, A. S. Federighi, G. H. Heinz, L. F. Stickel, and W. H. Stickel.

LITERATURE CITED

(*1*) *Barr, A. J., J. H. Goodnight, J. P. Sall, and J. T. Helwig. 1976.* A user's guide to SAS 76. Statistical System Institute, Raleigh, N.C. 329 pp.

(*2*) *Charnetski, W. A. 1976.* Organochlorine insecticide residues in ducklings and their dilution by growth. Bull. Environ. Contam. Toxicol. 16(2):138–144.

(*3*) *DeGurse, P., and V. Duter. 1975.* Chlorinated hydrocarbon residues in fish from major waters of Wisconsin. Wisconsin Department of Natural Resources, Fish Management Section Rept. No. 79. 21 pp.

(*4*) *DeGurse, P., and J. Ruhland. 1972.* Occurrence of chlorinated biphenyls in Mississippi River fish. Wisconsin Department of Natural Resources, Fish Management Rept. No. 52. 13 pp.

(*5*) *Mauck, W. L., and L. E. Olson. 1977.* Polychlorinated biphenyls in adult mayflies (*Hexagenia bilineata*) from upper Mississippi River. Bull. Environ. Contam. Toxicol. 17(4):387–390.

(*6*) *Minnesota-Wisconsin PCB Interagency Task Force. 1976.* Polychlorinated biphenyls (PCBs) in the Upper Mississippi River Basin. Minnesota Pollution Control Agency, Roseville, Minn. 55 pp.

(*7*) *Ohlendorf, H. M., E. E. Klaas, and T. E. Kaiser. 1978.* Environmental pollutants and eggshell thinning in the black-crowned night heron. Pp. 63–82 *in* A Sprunt, IV, J. C. Ogden, and S. Winckler, eds. Wading Birds National Audubon Research Rept. No. 7. National Audubon Society, New York, N.Y.

(*8*) *Ohlendorf, H. M., E. E. Klaas, and T. E. Kaiser. 1978.* Organochlorine residues and eggshell thinning in anhingas and waders. Pp. 185–195 *in* W. E. Southern, compiler. Proc. 1977 Conf. Colonial Waterbird Group. National Audubon Society, Tavernier, Fla.

(*9*) *Ohlendorf, H. M., E. E. Klaas, and T. E. Kaiser. 1978.* Organochlorine residues and eggshell thinning in wood storks and anhingas. Wilson Bull. 90(4):608–618.

(*10*) *Ohlendorf, H. M., E. E. Klaas, and T. E. Kaiser. 1979.* Environmental pollutants and eggshell thickness: anhingas and wading birds in the eastern United States. Fish and Wildlife Service Special Scientific Rept.–Wildlife No. 216, U.S. Department of the Interior, Washington, D.C.

(*11*) *Palmer, R. S., ed. 1962.* Handbook of North American Birds, Vol. 1, Loons through Flamingos. Yale University Press, New Haven, Conn. 567 pp.

(*12*) *Scheffé, H. 1959.* The Analysis of Variance. John Wiley & Sons, Inc., New York, N.Y. 477 pp.

(*13*) *Welty, J. C. 1963.* The Life of Birds. Alfred A. Knopf, Inc., New York, N.Y. 546 pp.

WATER

Herbicide Contamination and Decontamination of Well Waters in Ontario, Canada, 1969–78 [1]

Richard Frank, George J. Sirons, and Brian D. Ripley

ABSTRACT

Over the 10-year period 1969–78, the waters of 237 wells were analyzed because of contamination from herbicide spillage in or near the well, complaints of impaired water flavor, or injury to seedling plants moistened with the well water. Herbicides were identified in 159 wells: 98 had a single herbicide, 46 had two, 12 had three, one had four, and another had five separate herbicides contributing to the contamination. Wells were grouped according to the mode of entry of the contaminant. Entry occurred most commonly as an aerial spray drift or in runoff. Serious contaminations were caused by spillage of herbicide concentrates and spray solutions in or around the well.

Twenty-four of the contaminated wells were further investigated to determine the persistence of the contaminant and how to remove it. Some wells were decontaminated adequately to allow reuse within nine weeks, others required three years, and yet others had to be abandoned. Particularly persistent contaminants were amitrole, dinoseb, and picloram.

Introduction

In Ontario, water for spraying herbicides is drawn from wells, ponds, ditches, and creeks. The normal procedure is to fill the spray equipment directly from a water source, although filling from a nurse tank is quite common. According to the Pesticide Act of 1973, an anti-backflow device should be used when drawing from public waters. Mixing of the herbicides is advisably performed away from the water source. These procedures are not always followed, and as a result a number of wells have become contaminated with herbicides. In some cases, this has had detrimental effects when the well water was applied to seedling plants. In addition, herbicide treatment of croplands and weeds in close proximity to the well have impaired the water flavor.

Over the past 10 years, the Ontario Ministry of Agriculture and Food and the Ontario Ministry of the Environment have offered an analytical service to investigate well contaminations and to advise on cleanup. Records have been maintained on many of the wells to determine how long it took the owners to decontaminate their wells.

In the present study, 237 wells suspected of contamination were sampled and analyzed between 1969 and 1978.

Methods and Materials

SAMPLING

Field staff of the Ontario Ministries of Agriculture and Food and of the Environment responded to requests to sample wells where herbicide contaminations were known or suspected. Composite water samples were collected from several pumpings, and 1-liter quantities, for each herbicidal group suspected, were collected at the time of sampling. Repeated water sampling occurred until the well had been decontaminated or until the well was abandoned for a new one.

Water sampling was often part of a larger investigation into sources of plant injury especially where well water had been used to raise seedlings in a greenhouse. More often, herbicide spills had occurred into or around the well while water was being drawn for a spray operation; often humans and/or animals used the same water for drinking purposes. In many other cases, contamination was suspected when weeds had been sprayed near the well.

In some cases, single analyses were performed where the contamination was known. In others, multiple analyses were performed before the contaminants could be identified. Follow-up analyses were performed concomitant with the owners' attempts to decontaminate the wells.

ANALYSES

One-liter water samples were extracted within 24 hours of receipt by the laboratory. The procedures for extrac-

[1] Provincial Pesticide Residue Testing Laboratory, Ontario Ministry of Agriculture and Food, c/o University of Guelph, Guelph, Ontario, Canada N1G 2W1.

TABLE 1. *Analytical procedures followed for determining herbicides in well water samples, Ontario, Canada—1969–78*

Herbicides	Extracting Solvent	Cleanup	Quantification [1]	Recovery, %	References
Amitrole	none	ion-exchange	colorimetry	83	(9)
Bipryridyl	none	ion-exchange	colorimetry	90	(1)
Thiocarbamates	isooctane	none	GLC–FPD (sulfur)	95	(3)
Chlorinated phenols	benzene	methylation Florisil	GLC–ECD	95	(8)
Dalapon	diethyl ether	none	GLC–ECD	90	(4)
Dinitrophenols	benzene	Florisil	methylation GLC–ECD	96	(11)
Phenoxy and benzoic acids	chloroform	Methylation Florisil	GLC–ECD	95	(10)
Phenylureas	*n*-hexane	hydrolysis distillation	GLC–CCD	90	(2)
Picloram	diethyl ether	none	methylation GLC–ECD	90	(6)
Triazines	chloroform	none	GLC–CCD	95	(7)

[1] GLC = gas-liquid chromatography, FPD = flame photometric detection, ECD = electron-capture detection, CCD = Coulson conductivity detection.

tion, isolation, and quantitation of the 10 herbicide groups essentially followed the references presented in Table 1 with only minor revision. Identities were confirmed by the techniques given in the references or by use of alternative detection systems or different column packings in the gas-liquid chromatographic column.

Results

Between 1969 and 1978, 237 wells were sampled in 45 counties and districts throughout the Province of Ontario. The occurrence by region was 107 from the south, 54 from the west, 43 from the central, 21 from the east, and 12 from the north (Fig. 1). During the 10-year period, 505 samples were analyzed as follows: 161 for triazine, 204 for phenoxy and benzoic acids and chlorinated phenols, 39 for picloram, and 101 for a number of other herbicide groups (Table 2).

Where herbicides were used near the well, no identifiable contaminant could be found in 78, or 33 percent, of the wells (Table 2). In almost all cases of noncontamination, herbicides had been spilled or were noticed near the well. However, personnel applying

FIGURE 1. *Counties, districts, and regions of Ontario*

TABLE 2. *Farm and private rural wells analyzed for herbicide contamination, Ontario, Canada—1969–78*

Year of Initial Samples	Number of Wells Sampled	Number of Wells Free of Herbicides	Number of Wells Contaminated	Investigation: Number of Samples	Investigation: Number of Analyses
1969	9	1	8	11	11
1970	12	5	7	13	13
1971	19	8	11	22	24
1972	32	11	21	35	43
1973	27	4	23	47	58
1974	31	4	27	42	45
1975	35	12	23	87	108
1976	19	10	9	39	56
1977	35	13	22	56	75
1978	18	10	8	41	72
Total	237	78	159	393	505

the herbicides could not be sure whether the herbicides had actually entered the well, although soil near the well was contaminated.

Atrazine and 2,4-D were the herbicides reportedly spilled in about half the cases. Most of the remainder involved herbicides closely related to these two.

In 159, or 69 percent, of the wells, contaminants were positively identified. In 98 wells, a single ingredient was detected; in 46, two herbicides were found; in 12, three herbicides were found; and in one well each, four and five herbicides were present (Table 3). Twenty-two different herbicides were identified with levels of contamination covering eight orders of magnitude, i.e., 0.01 μg/liter to 150 mg/liter (Table 4).

Wells ranged in depth from sand points of 2.5 m to drilled wells of up to 40 m.

MODE OF ENTRY

From the investigations conducted on each site it was possible to divide the contaminations into five distinct types, depending on the mode of entry of the herbicides:

Type I—Herbicide concentrate entered the well as: IA, a single spill event directly into the water; or IB, an extended spill event that entered the water directly and indirectly.

Type II—Diluted herbicide solutions entered the well as: IIA, a single spill event directly into the water especially as back-siphoning from spray equipment; or IIB, an extended spill event which included direct and indirect entry into water especially where spray equipment was overfilled, or tanks were emptied or rinsed.

Type III—Herbicide drift entered the well during the spraying of vegetation adjacent to the well. This situation occurred especially where wells were located close to rights-of-way or where farmers sprayed weeds around their wells.

Type IV—Herbicide residues entered the well during storm runoff events as: IVA, rainwater carrying herbicides from past spills near the well; or IVB, rainwater carrying residues from recently treated fields or vegetation adjacent to the well.

TABLE 3. *Identity of herbicides contaminating 159 of 237 farm and private wells in Ontario, Canada—1969–78*

Number of Incidences of Each Herbicide Combination	Total Number of Wells Contaminated	Herbicides
SINGLE CONTAMINANT		
32	32	atrazine
23	23	2,4-D
17	17	PCP
5	5	2,4,5-T
4	4	picloram
3	9	amitrole, dinoseb, pebulate
2	2	paraquat
1	6	alachlor, butylate, dalapon, dicamba, MCPA, simazine
Subtotal	98	
TWO CONTAMINANTS		
12	12	2,4-D/2,4,5,-T
5	5	atrazine/alachlor
3	6	atrazine/simazine; 2,4-D/PCP
2	18	atrazine/cyanazine; atrazine/2,4-D; atrazine/PCP; atrazine/2,4,5-T; 2,4-D/dicamba; 2,4-D/dichlorprop; 2,4-D/fenoprop; 2,4-D/mecoprop; dicamba/fenoprop
1	5	2,4-D/TCA; dicamba/PCP; dinoseb/PCP; 2,4,5-T/PCP; linuron/prometone
Subtotal	46	
THREE CONTAMINANTS		
2	4	2,4-D/dicamba/mecoprop; 2,4-D/picloram/PCP
1	8	atrazine/2,4-D/simazine; atrazine/2,4-D/2,4,5-T; 2,4-D/dinoseb/PCP; 2,4-D/2,4,5-T/fenoprop; 2,4-D/2,4,5-T/PCP; 2,4-D/mecoprop/PCP; 2,4,5-T/fenoprop/PCP; dicamba/fenoprop/mecoprop
Subtotal	12	
FOUR CONTAMINANTS		
1	2	2,4-D/dinoseb/mecoprop/PCP 2,4,5-T/fenoprop/mecoprop/PCP
Subtotal	2	
FIVE CONTAMINANTS		
1	1	2,4-D/dicamba/fenoprop/MCPA/ mecoprop
Subtotal	1	
Grand total	159	

Type V—Subterranean movement into a well from normally used or spilled herbicides.

Well water contained herbicide residues that ranged from 0.01 μg/liter to 150 mg/liter and these were grouped according to initial concentrations (Table 4). The initial concentrations of Type I and II contaminations ranged from 0.1 μg/liter to a high of 14.6 mg/liter for 2,4-D. On the other hand, initial concentrations of Type III contaminations ranged from 0.01 to 370 μg/liter for 2,4-D and Type IV from 0.01 to 300 μg/liter for atrazine. Only picloram could be identified as a Type V contamination. In this latter case, residues ranged from 0.1 to 1.5 μg/liter. Where indirect con-

tamination occurred, the residues in water were below 400 μg/liter compared to the much higher residues of up to 150 mg/liter that occurred from direct contamination. Type III and IV contaminations occurred most frequently and reflected the closeness to wells that herbicides had been sprayed; in general, herbicides were hormone-types applied to existing vegetation, or other types applied pre-emergence to cropland (Table 5).

CASE HISTORIES

Twenty-four case histories are given in Table 6. Only those wells for which details of the mode-of-entry and

TABLE 4. *Number of herbicides by concentration and type of entry among 159 wells found contaminated in Ontario between 1969–78*

	Concentration, μg/Liter, and Number of Wells Contaminated and Type of Entry [1]							
Herbicide	0.01–0.1	0.1–1.0	1.1–10	11–100	101–1,000	1,001–10,000	10,000–+	Total
2,4,-D	3(III–IV)	28(II–IV)	12(II–IV)	10(I–III)	6(I–III)[2]	1(I)	1(II)[3]	61
Atrazine	0	21(II–IV)	7(II–IV)	6(I–IV)	11(I–IV)[4]	4(I,II)	1(I)[5]	50
Chlorinated phenols	12	16	4	1(I)	0	0	0	33
2,4,5-T	0	13(III, IV)	7(II–IV)	3(I–III)	1(I)	1(II)	0	25
Dicamba	1(IV)	5(III,IV),	1(IV)	1(II)	1(II)	1(I)	0	10
Fenoprop	0	6(III)	0	2(II)	1(I)	0	0	9
Mecoprop	2(III)	2(III)	0	4(II,III)	0	0	1(I)[6]	9
Dinoseb	2(III)	0	1(IV)	1(IV)	1(II)	1(I)	0	6
Picloram	0	3(III,V)	2(IV,V)	1(III)	0	0	0	6
Alachlor	0	1(IV)	2(IV)	0	2(II)	1(II)	0	6
Simazine	0	3(IV)	1(II)	0	0	0	1(II)[7]	5
Amitrole	0	1(III)	0	0	0	2(II)	0	3
Pebulate	0	0	3(IV)	0	0	0	0	3
Cyanazine	0	1(IV)	1(II)	0	0	0	0	2
Dichlorprop	0	0	1(III)	0	1(II)	0	0	2
MCPA	0	0	1(III)	0	0	1(I)	0	2
Paraquat	0	0	0	1(II)	0	1(I)	0	2
Butylate	0	1(II)	0	0	0	0	0	1
Dalapon	0	1(II)	0	0	0	0	0	1
Linuron	0	0	1(IV)	0	0	0	0	1
Prometone	0	0	0	1(II)	0	0	0	1
TCA	0	1(IV)	0	0	0	0	0	1
Total	20	103	44	31	24	13	4	239

[1] Type of entry: I, concentrated herbicide; II, diluted herbicide; III, drift during spraying; IV, during storm runoff; V, subterranean.
[2] Highest Type III, 370 μg/liter 2,4-D.
[3] Highest Type I and II contamination, 14.6 mg/liter 2,4-D.
[4] Highest Type IV, 300 μg/liter atrazine.
[5] Highest contamination was 22.4 mg/liter.
[6] Highest contamination was 150 mg/liter.
[7] Highest contamination was 12.6 mg/liter.

TABLE 5. *Number of herbicides involved in the five types of well contaminations, Ontario, Canada, 1969–78*

	Type of Entry [1]					
	I	II	III	IV	V	Total
Herbicide	Number of Contaminants					
2,4-D	5	6	22	28	0	61
Atrazine	1	16	8	25	0	50
Chlorinated phenols [2]	1				0	33
2,4,5-T	2	3	18	2	0	25
Dicamba	1	2	5	2	0	10
Fenoprop	1	2	6	0	0	9
Mecoprop	1	1	7	0	0	9
Dinoseb	1	1	2	2	0	6
Picloram	0	0	3	1	2	6
Alachlor	0	4	0	2	0	6
Simazine	0	2	0	3	0	5
Amitrole	0	2	1	0	0	3
Pebulate	0	0	0	3	0	3
Cyanazine	0	1	0	1	0	2
Dichlorprop	0	1	1	0	0	2
MCPA	1	0	1	0	0	2
Paraquat	1	1	0	0	0	2
Butylate	0	1	0	0	0	1
Dalapon	0	1	0	0	0	1
Linuron	0	0	0	1	0	1
Prometone	0	1	0	0	0	1
TCA	0	0	0	1	0	1
Total	15	(45)	(74)	(71)	(2)	239

[1] Type of entry: I, concentrated herbicide; II, diluted herbicide; III, drift during spraying; IV, during storm runoff; V, subterranean.
[2] Source and modes of entry not determined.

TABLE 6. *Case histories of 24 farms with private wells investigated for herbicide contamination, Ontario, Canada—1969–78*

Case No.	Well	Herbicide Spill	Days After Contamination	Concentration µg/Liter	Impact	Well Cleanup
			IA. HERBICIDE CONCENTRATE ENTERED WELLS DIRECTLY			
1	Drilled, 20 m	50 ml 50 percent 2,4-D amine from container, May 1974	0 316 375	610 0.5 Reused	Killed or distorted tobacco seedlings	Pumped dry several times over one year.
2	Shallow, 3 m	2.5 liters each 35 percent 2,4-D and dichlorprop, August 1973	0 6 10 28 46 61	2,4-D dichlorprop 140 240 1,350 4,660 100 960 0.2 0.4 Reused	Impaired water flavor	Emptied three times, 15,000 liters Pumped continually for 4 weeks, walls washed.
3	Shallow 4 m deep	50 ml 50 percent 2,4-D amine, May 1977	0 64 132	780 5.6 Reused	Killed greenhouse plants	Pumped dry intermittently for 4 months.
			IB. HERBICIDE CONCENTRATE ENTERED WELLS DIRECTLY AND INDIRECTLY			
4	Sand point, 4 m	23 liters 36 percent dinoseb from container, May 1973	0 52 86 111 237 285	2,330 2,240 61 72 150 3,800	Killed tobacco seedlings	Pumped until yellow color disappeared; color returned and pumping continued. Spring thaw water deep yellow.
5	Cased well, 22 m	50 ml 60 percent 2,4,5-T from container, August 1975	Well abandoned 0 86 1,028	26.3 5.5 Not used	Impaired water flavor for 34 months	Pumped on and off for 6 months and abandoned.
			IIA. DILUTED HERBICIDES ENTERED WELLS DIRECTLY			
6	Drilled, 25 m	About 50 liters 1 percent solution atrazine back-siphoned, June 1974	0 1 11 68	— 610 barn, 1,840 house 9 barn, 29 house Reused	Continuously fed to swine with no visible effects.	Pumped continuously for 11 days, then intermittently.
7	Medium depth, 10 m	About 25 liters 1 percent solution atrazine back-siphoned, June 1977	0 2 8 21 49 64	— 833 50 14 5.7 Reused	Stopped use for livestock and house	Pumped continually for about 60 days. Well sides scraped.
8	Shallow, 4.5 m	About 100 liters 1 percent solution atrazine back-siphoned, June 1977	0 2 32 338	— 6,670 212 Reused	Stopped use for livestock and house	Pumped dry once and sampled. Pumped continually for 30 days. Periodically pumped for nine months.
9	Drilled, 17 m	Unknown quantity of atrazine/alachlor mixture back-siphoned, May 1975	0 1 3 64 0	— — 370 5,690 14 54 Reused	Stopped use for livestock and house	Pumped dry and sampled, continued pumping for five days and then intermittently for two months.
10	Drilled, 21 m	About 100 liters of 1 percent solution of atrazine–alachlor backsiphoned, June 1978	13 47 160	4,040 5,690 1,031 1,827 90 130 Reused	Continued use for cattle; stopped use for humans	Pumped continuously for 47 days then intermittently.
11	Sand point, 5 m	About 50 liters of 1.5 percent solution of amitrole back-siphoned, April 1974	0 11 67 358 1,092	Reused 1,320 540 50	Killed all tobacco seedlings in greenhouse after well was pumped dry once	Pumped dry intermittently for over two years.
12	Sand point, 5 m	About 1 liter of 1 percent solution of picloram back-siphoned, May 1976	0 130 450 706 749	— 7.2 1.7 0.08 Reused	Tobacco seedlings wiped out initially; at 706 days, seedlings still affected	Pumped dry continually first year then intermittently second year. Pumped continually for 50 days before reuse.
			IIB. DILUTED HERBICIDES ENTERED WELLS DIRECTLY OR INDIRECTLY			
13	Medium depth, 9 m	Atrazine from an over-filled sprayer spilled around the lip of the well and into well, May 1976	0 4 100 110	1,792 67 ND Reused	Vegetation around well killed.	Well pumped dry, scraped, and sediment removed.
14	Drilled, 10 m	Spray tank containing a mixture of 3 percent 2,4-D/ dicamba was spilled around well, July 1977	0 2 32 39 49 70 95 294	93 90 600 267 447 35 71 ND 374 49 4.5 4.8 Reused	Domestic use stopped; water flavor impaired	Pumped out 35 times in 4 months, then emptied periodically.

(*Continued next page*)

TABLE 6. (Cont'd.) *Case histories of 24 farms with private wells investigated for herbicide contamination, Ontario, Canada—1969–78*

Case No.	Well	Herbicide Spill	Days After Contamination	Concentration µg/Liter	Impact	Well Cleanup
			IIB. DILUTED HERBICIDES ENTERED WELLS DIRECTLY OR INDIRECTLY (*Cont'd.*)			
15	Shallow, 4 m	Spray tank of 1.5 percent solution dicamba spilled around well	0 48 220 272 570 617	60 4.2 1.2 11.3 3.5 <0.1	Tobacco seedlings wiped out or injured two years in a row	Pumped out regularly at first then periodically. New well dug nearby.
			abandoned for new well of 8 m deep			
16	Sand point, 2.5 m	Most of 900-liter tank of 1.5 percent amitrole, April 1975	0 30 71 109 192 441 723 1,093	— 2,800 1,100 800 610 30 40 3 (reused)	Tobacco seedlings wiped out for over 2 years	
			III. AERIAL HERBICIDE DRIFT ENTERED WELLS			
17	Shallow, 3.5 m	2,4-D drift of 1 percent solution, June 1974	0 4 38 78	— 370 ND Reused	Water flavor impaired	Well emptied three times after detection of residue.
18	Shallow, 4 m	A 1 percent solution of 2,4-D/2,4,5-T drifted 7.5 m from rights of way, June 1975	0 2 16 20	— 42 <0.1 Reused	— 34 <0.1	Water flavor impaired Well emptied twice after detection.
			IV. HERBICIDES ENTERED WITH RUNOFF			
19	Sand point, 2.5 m	Heavy rains carried atrazine from spill near well, June 1969	0 103 281	22 15 ND	Killed tobacco seedlings	Occassionally pumped dry over nine months.
20	Sand point, 2.5 m	Spring thaw carried atrazine and desethyl atrazine from adjacent field, April 1973	0 389	15 1	22 2	Continued use for livestock Emptied well once.
21	Shallow, 4.5 m	Storm runoff carried atrazine and metabolite from treated field, May 1975	0 50 134 379	0.4 6.4 1.2 0.4	0.1 2.1 2.2 1.6	Continued use for livestock Emptied several times in first year.
22	Shallow, 4.5 m	Storm runoff carried atrazine and metabolite from treated field, October 1977	0 38 173	0.6 ND Reused	4.6 ND	Stopped use for livestock
23	Shallow, 5.0 m	2,4-D linked to runoff from weeds treated around well, October, 1971	0 158 205 227	— 2.5 1.6 ND Reused		Killed seedlings during Spring 1972 Pumped regularly over two-month period with no pesticides detected.
			V. SUBTERRANEAN MOVEMENT OF HERBICIDES INTO WELL			
24	Shallow, 4 m	Picloram used some distance from well, surplus dumped nearby, June 1974	0 287 301 333 344 357 370 377 386 411 414 420 435 439 493 498 523 704 781 1,040 1,101	— 1.5 0.2 7.5 & 10.9 3.0 & 5.9 0.8 0.6 0.3 2.3 0.2 0.3 0.3 0.3 <0.1 0.4 0.7 0.2 ND 0.4 0.4 ND	Killed seedlings during spring 1975 and each year until 1977. Abandoned June 1977	Pumped intermittently between Spring 1975 and June 1977.

NOTE: ND = none detected.

decontamination procedures could be clearly documented have been chosen.

Type IA, herbicide concentrates entered wells directly. Three cases are cited in Table 6. In one, a container stored over a well leaked into the water; in the other two, herbicide concentrate was spilled into the well during handling. In all three cases, decontamination was difficult until the sides of the well were scraped and cleansed of spilled herbicide. Even after the well was pumped dry once or twice, large numbers of plant seedlings were killed in two instances because the decontamination had been inadequate. Only continued pumping over an extended period removed the contamination.

Type IB, herbicide concentrate entered wells directly and indirectly. Two cases are cited in Table 6; in both, the concentrate leaked from containers stored near the well. In one case, dinoseb soaked into the ground around the well as well as running directly into the well. During the spring thaw and runoff period, when the ground was saturated with water, dinoseb entered with runoff and drainage waters to seriously contaminate the well for a second year. In the second case, 2,4,5-T leaked behind the casing of the well and impaired the water flavor for 34 months after the event.

Type IIA, diluted herbicide entered wells directly. Seven cases are cited and all involved accidental back-siphoning of diluted solutions of herbicides into the wells (Table 6). Cleanup involved pumping out water with existing small equipment that emptied the wells slowly. Decontamination took as little as two months in some wells but as long as two to three years in others.

Type IIB, diluted herbicides entered wells directly or indirectly. Four cases were investigated, and in all, the herbicides were spilled into and around the well mouth while spray equipment was being filled (Table 6). The contaminated water severely damaged seedling plants in greenhouses before it was adequately decontaminated. Cleanup operations involved pumping water out of the wells during an extended period of 100–1093 days. In the one well that was decontaminated in 100 days, the walls and the bottom of the well were scraped and the soil and sediment were removed.

Type III, aerial herbicide drift entered wells. Two wells were investigated in which aerial drift of chlorophenoxy herbicides had entered the water and impaired its flavor. Both wells were located within 7 to 10 m of the treated areas. Cleanup was effected in two to five weeks by emptying the well two to three times.

Type IV, herbicides entered with storm water runoff. Five cases are cited in Table 6. Heavy rains producing runoff carried atrazine into well water from a spill near the well that had occurred 10 days before the rains. In three other cases, atrazine from treated corn fields 4–15 m from the wells was deposited in the wells by storm runoff waters. In one other case, heavy rains washed 2,4-D into well water from recently sprayed tall weeds adjacent to the well. Seedling plants were destroyed following the use of water from these contaminated wells. Two farmers continued to use the contaminated water for livestock when it was discovered that atrazine levels were relatively low. No adverse effects among animals were reported. Four of the five wells were decontaminated in periods ranging from 38 days to just over one year.

Type V, subterranean movement of herbicides into wells. Continued distortion of plant seedlings moisturized for three years by water from a well could only be explained by the subterranean movement of picloram. Picloram had been used to spray vegetation some distance from the well, and the unused portion was dumped in the same area. A possible connection between the well and the treated site was an aquifer close to the surface.

Discussions and Conclusions

Use or misuse of herbicides around wells resulted in contamination of 67 percent of the examined wells. In 159 wells, 22 herbicides were found as single or multiple contaminants, for 239 individual contamination events. Contamination levels were greatest where concentrated or diluted spray solutions were spilled directly into the well. However, these were not necessarily the most difficult to decontaminate. The mode-of-entry did influence the time required for decontamination. Contaminants entering as drift were relatively rapidly removed compared to subterranean contaminants which were particularly persistent in spite of their initial low levels.

Schneider et al. (*5*) found that both atrazine and picloram moved freely through an aquifer to contaminate wells 9 m and 20 m away but not 45 m from the injection site. Up to 90 percent of the injected herbicides were recovered. Picloram took 84 hours to arrive in the well 20 m from the injection. Concentrations increased and decreased over the pumping period of 12 days, reaching a high of 135 ppb (*5*) when pumping rates were 82 m^3/hour. The picloram concentrations were considerably more attenuated in the case of subterranean movement reported in the present paper, and the distance from the area of use to the well was several hundred meters. Few wells in the present study were pumped continuously day and night for extended periods or at the high rates available to Schneider et al. (*5*). These differences probably explain why cleanup took so much longer in the present study.

Where herbicide was spilled down the wall of the well (case 2), and/or around the lip of the well (cases 14 and 15), concentrations first declined and then increased as more herbicide entered the water. In case 2, residues in water rapidly declined after the walls had been scraped. In case 4, dinoseb was spilled in quantity

around a well, and it soaked into the soil where it remained with little movement as long as the soil was moist to dry. However, during the spring thaw, the soil was saturated with water and the herbicide leaked into the well (case 4). Atrazine continued to degrade in one well (case 21) where the ratio of atrazine to metabolite was 4:1 in May 1975 and 1:4 in June 1976.

The type of compound involved had an important bearing on the time required for decontamination. Amitrole, dinoseb, and picloram were particularly difficult to remove from water supplies, but alachlor, atrazine, and 2,4-D were removed more rapidly.

Emptying the well of water was not always possible. When the well could be emptied, cleanup was facilitated by removing soil around the well or from the sides or bottom of the well. In cases 2, 7, and 13, the wells were emptied, and contaminated soils and sediments were removed. Hence decontamination was rapid, i.e., 61–100 days. Where only water was removed, decontamination took 20–1093 days. It should be pointed out that owners followed their own procedures for well decontamination. The combination of differences in well depths, soil types, refilling rates, and initial herbicide concentrations make most of the 159 contaminated wells unique events. Hence the decontamination of 24 wells makes it difficult to generalize on the best practical procedures.

Acknowledgments

The authors thank the fields staffs of the Ontario Ministry of Agriculture and Food and the Ontario Ministry of the Environment for supplying the samples and information on the wells discussed in this paper.

LITERATURE CITED

(*1*) *Calderbank, H., and S. H. Yuen. 1965.* An ion exchange method for determining paraquat residues in food crops. Analyst 90(1067):99–106.

(*2*) *Dalton, R. L., and H. L. Pease. 1962.* Determination of residues of diuron, monuron, fenuron, and neburon. J. Assoc. Off. Agric. Chem. 45(2):377–381.

(*3*) *Frank, R., H. E. Braun, G. J. Sirons, M. V. H. Holdrinet, B. D. Ripley, D. Onn, and R. Coote. 1978.* Stream flow quality—Pesticides in 11 agricultural watersheds in southern Ontario, Canada, 1974–77. International Reference Group on Great Lakes Pollution from Land Use Activities, International Joint Commission, Windsor, Ontario.

(*4*) *Getzendaner, M. E. 1969.* Gas chromatographic determination of residues of dalapon in several substrates. J. Assoc. Off. Anal. Chem. 52(4):824–831.

(*5*) *Schneider, A. D., A. F. Wiese, and O. R. Jones. 1977.* Movement of three herbicides in a fine sand aquifer. Agron. J. 69(3):432–436.

(*6*) *Sirons, G. J., R. Frank, and R. M. Dell. 1977.* Picloram residues in sprayed MacDonald-Cartier Freeway right-of-way. Bull. Environ. Contam. Toxicol. 18(5): 526–533.

(*7*) *Sirons, G. J., R. Frank, and T. Sawyer. 1973.* Residues of atrazine, cyanazine, and their phytotoxic metabolites in a clay loam soil. J. Agric. Food Chem. 21(6): 1016–1020.

(*8*) *Sirons, G. J., and Y. J. Paik. 1978.* Extraction and quantitation of chlorinated phenols in aquatic substrates. Presented at International Symposium for the Analysis of Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, May, Hamilton, Ontario, Canada.

(*9*) *Sutherland, G. L. 1964.* 3-Amino-s-triazole. *In* Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives. G. Zweig., Ed., Vol. IV, Chapt. 3, Academic Press, New York, N.Y.

(*10*) *Yip, G. 1971.* Improved method for determination of chlorophenoxy acid residues in total diet samples. J. Assoc. Off. Anal. Chem. 54(4):966–969.

(*11*) *Yip, G., and S. F. Howard. 1968.* Extraction and cleanup procedure for the gas chromatographic determination of four dinitrophenolic pesticides. J. Assoc. Off. Anal. Chem. 51(1):24–28.

Triazine Herbicide Residues in Central European Streams [1]

W. D. Hörmann,[2] J. C. Tournayre,[3] and H. Egli[2]

ABSTRACT

Triazine herbicide residues were monitored in the rivers Adour, Danube, Garonne, Herault, Loire, Marne, Oise, Rhine, and Rhône from spring 1976 to fall 1977 to determine whether the continued use of the compounds resulted in accumulations of undesirable residues in the streams. Samples were generally collected monthly or bimonthly and analyzed for the parent compounds atrazine, simazine, terbumeton, terbuthylazine, and dealkylated metabolites GS 26571 (2-amino-4-tert-butylamino-6-methoxy-1,3,5-triazine) and G 30033 (2-amino-4-chloro-6-ethylamino-1,3,5-triazine). The compounds were extracted into dichloromethane and quantitated by gas chromatography (GC) with nitrogen-specific detection. Selected results were verified by GC with mass fragmentographic detection. Limit of detection was usually 0.4 mg/m³; 80 percent of all results were below 0.4 mg/m³, 14 percent were 0.4–1 mg/m³, 6 percent were 1–10 mg/m³, and 0.3 percent were higher than 10 mg/m³. Detectable residues were mainly atrazine from the downstream sampling sites. Residues usually peaked during June.

Introduction

Triazine compounds, especially atrazine, have been widely used as herbicides for many years. The compounds, under the trade names Gesatop, Gesaprim, and Caragard, mainly have been applied to maize, orchards, and vine. Because they might reach surface waters via runoff or even via leaching, residues of the compounds could accumulate in streams. To gather information about the actual residue situation in Central European streams draining the main cultivation regions of maize, vine, and fruits, a monitoring program was initiated in Austria, France, Germany, and Switzerland during spring 1976. Concentrations of the following compounds were monitored: atrazine, simazine, terbumeton, terbuthylazine, GS 26571 (2-amino-4-*tert*-butylamino-6-methoxy-1,3,5-triazine), and G 30033 (2-amino-4-chloro-6-ethylamino-1,3,5-triazine).

Water samples were collected monthly or bimonthly between spring 1976 and fall 1977. At each site a total of 6–12 samples were taken, which the authors felt would reasonably indicate the actual residue situation and the seasonal fluctuations.

[1] Presented in part at the Fourth International Congress of Pesticide Chemistry, IUPAC, Zurich, Switzerland, 1978.

[2] CIBA-GEIGY Ltd., Agricultural Division, 4002 Basel, Switzerland.
[3] CIBA-GEIGY SA, 30670 Aigues-Vives, France.

Three samples across the profile of a river were shown to result in the same average as did 10 samples. To reduce the effect of potential outliers, the number of samples, however, should not be less than three (L. Newby and B. G. Tweedy, CIBA-GEIGY Corp., Greensboro, North Carolina, private communication, 1976). Therefore the following procedure was chosen:

Ten-liter samples each were taken at a depth of about 50 cm from either bank and from the center of the river by means of a metal bucket. Two liters of each sample were combined and mixed. From the mixed samples, 1-liter aliquots were transferred into aluminum bottles, deep frozen, and shipped to the residue laboratory.

Until analysis, samples were stored at −20°C. Triazines stored at this temperature have been shown to be stable for many years in neutral aqueous solutions (*1*) as well as in soil and crop materials (*2*).

Depending on stream length, one to four sampling sites were selected. Locations are shown on the map in Figure 1. Information on drained area, upstream of each sampling site, and main cultures is given in Table 1.

Analytical Procedures

The entire contents of one bottle, 1 liter, was thawed and the water was filtered to remove sediments. The filtrate was transferred to a 2-liter separatory funnel, and extracted with three consecutive portions of dichloromethane which had been used previously to rinse the sample container. After passage over a plug of cotton to remove excess water, the extracts were combined and evaporated to dryness in a rotary evaporator, using a 30°C water bath. The residue was dissolved in an appropriate volume, 0.5–2 ml, of a 1:1 mixture of hexane-ethanol and the solution was injected into a gas chromatograph equipped with a nitrogen-specific Hall or Coulson detector. Instrument parameters and operating conditions follow:

Columns:	glass, 1 m long × 3 mm ID packed with either 3 percent Carbowax 20M on 0.15–0.18 mm Gas-Chrom Q or 2 percent FFAP on 0.15–0.18 mm Gas-Chrom G	
Temperatures:	injector	250°C
	columns	190°–210°C isothermal
	interface	250°C
	detector oven	800°C
Carrier gas:	helium flowing at 60 cm³/minute	

FIGURE 1. *Map showing location of sample sites along Central European streams—spring 1976–fall 1977 (see Table 1 for key)*

TABLE 1. *Sites on Central European rivers sampled for triazine herbicide residues, spring 1976–fall 1977*

Stream	Sampling Site [1]	Drainage Area, km²	Main Cultures	Remarks
Adour	1 Urt	17,000	maize vineyard fruits	main maize cultivation region of France
Danube	2 Deggendorf	39,000	fruits fodder crops vineyard	vineyard downstream of Deggendorf
Garonne	4 Le Mas d'Agenais	50,000	vineyard maize	
Herault	5 Bessan	2,300	vineyard	
Loire	6 St. Benoit	73,000	vineyard	
	7 Savennieres	110,000	fodder crops fruits	
Marne	8 Meaux	13,000	vineyard	Champagne
Oise	9 La Verberie	15,000	fodder crops fruits	
Rhine	10 Laufenburg	31,000	fodder crops	(L)[2] upstream of
	11 Augst	31,000	vineyard	CIBA-GEIGY pro-
	12 Basel	32,000	fruits	duction plants
	13 Mainz	94,000		(B)[2] downstream of plants
Rhone	14 Bouveret	5,400	vineyard	between (B)[2] and
	15 Geneve	8,000	fruits	(G)[2]: Lake of
	16 Donzere	67,000		Geneva, viticulture
	17 Pin Fourcat	95,000		at borders

[1] Numbers refer to Figure 1.
[2] Letters refer to Figure 1.

Minimum detection levels were 0.1–0.4 mg/m³ except in a few cases where relatively high concentrations of interfering materials were present. Recoveries for all compounds were 80–120 percent at 5 mg/m³ and 10 mg/m³ fortification levels.

Several samples showing residues above the detection limit were confirmed by gas chromatography/mass spectrometry. Instrument parameters and operating conditions follow:

Instrument:	Finnigan Model 3000, equipped with programmable multiple ion monitor	
Masses selected:	atrazine	215
	simazine	201
	terbumeton	225
Column:	glass, 1 m long × 2 mm ID, packed with 2 percent SP 1000 on 0.15–0.18 mm Chromosorb G	
Temperatures:	injector	240°C
	column	220°C isothermal
	separator	220°C
	transfer	180°C
	manifold	120°C
Electron energy:	70 eV	
Carrier gas:	helium flowing at 30 cm³/minute	

TABLE 2. *Number of samples from Central European streams, containing atrazine residues at four given mg/m³ ranges, spring 1976–fall 1977*

	Sampling Site [1]	<0.4	0.4–1.0	1.1–10	>10
1	Adour (Urt)	2	1	2	0
2	Danube (Deggendorf)	3	3	3	0
3	Danube (Hainburg)	0	1	4	2
4	Garonne (Le Mas d'Agenais)	1	2	2	0
5	Herault (Bessan)	2	3	0	0
6	Loire (St. Benoit)	2	3	1	0
7	Loire (Savennieres)	2	3	1	0
8	Marne (Meaux)	4	1	1	0
9	Oise (La Verberie)	2	3	1	0
10	Rhine (Laufenburg)	9	0	0	0
11	Rhine (Augst)	8	1	0	0
12	Rhine (Basel)	7	2	0	0
13	Rhine (Mainz)	1	2	0	0
14	Rhone (Bouveret)	12	0	0	0
15	Rhone (Geneve)	12	0	0	0
16	Rhone (Donzere)	1	1	2	0
17	Rhone (Pin Fourcat)	2	2	1	0

[1] Numbers refer to Figure 1.

Results and Discussion

Tables 2–6 present all values found, expressed as number of results within given concentration ranges of <0.4, 0.4–1.0, 1.1–10, and >10 mg/m³; values are not corrected for recovery. Where two or more sampling sites for the same river are listed, the upstream sampling sites are listed first. No table for G 30033 was included because no residues of the compound were found in any of the samples.

Of 708 values measured, two, or 0.3 percent, were above 10 mg/m³; 43, or 6.1 percent, were between 1.1 and 10 mg/m³; 98, or 13.8 percent, were between 0.4 and 1 mg/m³; and 565, or 79.8 percent, were below 0.4 mg/m³, showing that transfer from treated areas to the rivers via runoff or leaching is very small.

Where different sites of a river were sampled, samples from the downstream sites normally showed higher residues than did samples from the upstream sites.

Residue levels peaked in June (Fig. 2) as they did in similar studies in the United States (*3*) and Canada (*4*).

TABLE 3. *Number of samples from Central European streams, containing simazine residues at four given mg/m³ ranges, spring 1976–fall 1977*

	Sampling Site [1]	< 0.4	0.4–1.0	1.1–10	> 10
1	Adour (Urt)	0	4	1	0
2	Danube (Deggendorf)	9	0	0	0
3	Danube (Hainburg)	6	1	0	0
4	Garonne (Le Mas d'Agenais)	0	4	1	0
5	Herault (Bessan)	1	4	0	0
6	Loire (St. Benoit)	5	1	0	0
7	Loire (Savennieres)	4	2	0	0
8	Marne (Meaux)	5	1	0	0
9	Oise (La Verberie)	3	2	1	0
10	Rhine (Laufenburg)	9	0	0	0
11	Rhine (Augst)	9	0	0	0
12	Rhine (Basel)	6	3	0	0
13	Rhine (Mainz)	3	0	0	0
14	Rhone (Bouveret)	11	0	1	0
15	Rhone (Geneve)	12	0	0	0
16	Rhone (Donzere)	1	2	1	0
17	Rhone (Pin Fourcat)	2	1	2	0

[1] Numbers refer to Figure 1.

TABLE 4. *Number of samples from Central European streams, containing terbumeton residues at four given mg/m³ ranges, spring 1976–fall 1977*

	Sampling Site [1]	< 0.4	0.4–1.0	1.1–10	> 10
1	Adour (Urt)	1	3	1	0
2	Danube (Deggendorf)	9	0	0	0
3	Danube (Hainburg)	7	0	0	0
4	Garonne (Le Mas d'Agenais)	3	0	2	0
5	Herault (Bessan)	3	2	0	0
6	Loire (St. Benoit)	4	1	1	0
7	Loire (Savennieres)	5	0	2	0
8	Marne (Meaux)	3	2	1	0
9	Oise (La Verberie)	3	1	2	0
10	Rhine (Laufenburg)	9	0	0	0
11	Rhine (Augst)	9	0	0	0
12	Rhine (Basel)	8	1	0	0
13	Rhine (Mainz)	3	0	0	0
14	Rhone (Bouveret)	12	0	0	0
15	Rhone (Geneve)	12	0	0	0
16	Rhone (Donzere)	3	1	0	0
17	Rhone (Pin Fourcat)	2	2	1	0

[1] Numbers refer to Figure 1.

TABLE 5. *Number of samples, from Central European streams, containing terbuthylazine residues at four given mg/m³ ranges, spring 1976–fall 1977*

	Sampling Site [1]	< 0.4	0.4–1.0	1.1–10	> 10
1	Adour (Urt)	3	2	0	0
2	Danube (Deggendorf)	9	0	0	0
3	Danube (Hainburg)	4	1	2	0
4	Garonne (Le Mas d'Agenais)	2	2	1	0
5	Herault (Bessan)	5	0	0	0
6	Loire (St. Benoit)	5	1	0	0
7	Loire (Savennieres)	5	1	0	0
8	Marne (Meaux)	4	1	1	0
9	Oise (La Verberie)	5	1	0	0
10	Rhine (Laufenburg)	9	0	0	0
11	Rhine (Augst)	9	0	0	0
12	Rhine (Basel)	8	1	0	0
13	Rhine (Mainz)	3	0	0	0
14	Rhone (Bouveret)	12	0	0	0
15	Rhone (Geneve)	12	0	0	0
16	Rhone (Donzere)	4	0	0	0
17	Rhone (Pin Fourcat)	4	1	0	0

[1] Numbers refer to Figure 1.

TABLE 6. *Number of samples from Central European streams, containing GS 26571 residues at four given mg/m³ ranges, spring 1976–Fall 1977*

	Sampling Site [1]	< 0.4	0.4–1.0	1.1–10	> 10
1	Adour (Urt)	1	3	1	0
2	Danube (Deggendorf)	9	0	0	0
3	Danube (Hainburg)	7	0	0	0
4	Garonne (Le Mas d'Agenais)	0	5	0	0
5	Herault (Bessan)	3	2	0	0
6	Loire (St. Benoit)	6	0	0	0
7	Loire (Savennieres)	4	1	1	0
8	Marne (Meaux)	4	1	1	0
9	Oise (La Verberie)	3	2	1	0
10	Rhine (Laufenburg)	9	0	0	0
11	Rhine (Augst)	9	0	0	0
12	Rhine (Basel)	9	0	0	0
13	Rhine (Mainz)	3	0	0	0
14	Rhone (Bouveret)	12	0	0	0
15	Rhone (Geneve)	12	0	0	0
16	Rhone (Donzere)	0	4	0	0
17	Rhone (Pin Fourcat)	2	3	0	0

[1] Numbers refer to Figure 1.

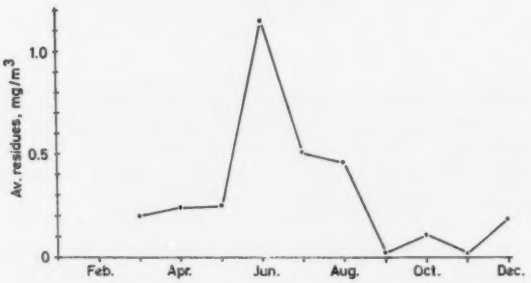

FIGURE 2. *Sum of the concentration of all compounds analyzed by month. Values below the limit of determination were taken as zero.*

This maximum must be caused by runoff after spring herbicide applications, because leaching of compounds would have resulted in more delayed and more constant residues. River volumes could not account for the June peak, because rivers rising in the Alps show their greatest volumes in June when snow melts. The resulting water volumes should dilute residues, thereby causing a June minimum. So, river volumes influence the residue situation only to a small extent. The main contribution to the June peak obviously comes from runoff within a short time after application.

The results from Laufenburg, upstream of two triazine production plants, from Augst, in between the plants, and from Basel, downstream of both plants, demonstrate that residues are not increased by those plants.

Where residues were present at all, those of atrazine were highest. This was expected because atrazine is the most commonly used triazine herbicide. From this fact, the conclusion can be drawn that in future monitoring programs it is sufficient to analyze only for atrazine as a tracer.

LITERATURE CITED

(*1*) *Burkhard, N., and J. A. Guth. 1978.* Chemical hydrolysis of 2-chloro-4,6-bis(alkylamino)-1,3,5-triazine herbicides and their breakdown in soil under the influence of absorption. Abstr. Vol. Fourth International Congress of Pesticide Chemistry, IUPAC, Zürich, Switzerland. Abstr. No. V–605.

(*2*) *Egli, H., and N. Burkhard. 1978.* Deep freeze stability of some pesticide residues in biological material and soil. Abstr. Vol. Fourth International Congress of Pesticide Chemistry, IUPAC, Zürich, Switzerland. Abstr. No. VI–707.

(*3*) *Frank, R., and G. J. Sirons. 1978.* Atrazine: Its use and entry into stream water. Abstr. Vol. Fourth International Congress of Pesticide Chemistry, IUPAC, Zürich, Switzerland, Abstr. No. VI–815.

(*4*) *Newby, L., and B. G. Tweedy. 1976.* Atrazine residues in major rivers and tributaries. 172nd Meeting, American Chemical Society, Abstr. Papers PEST 102.

APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALACHLOR	2-Chloro-2′,6′-diethyl-*N*-(methoxymethyl)-acetanilide
AMITROLE	3-Amino-*s*-triazole
AROCLOR 1254	PCB, approximately 54% chlorine
ATRAZINE	2-Chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine
AZODRIN	Dimethyl phosphate of 3-hydroxy-*N*-methyl-*cis*-crotonamide
BHC (Benzene Hexachloride)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers)
BOTRAN	2,6-Dichloro-4-nitroaniline
BUTYLATE	*S*-Ethyl diisobutylthiocarbamate
CARBARYL	1-Naphthyl methylcarbamate
CIPC	Isopropyl *N*-(3-chlorophenyl)carbamate
CYANAZINE	2-[[4-Chloro-6-(ethylamino)-*s*-triazin-2-yl]amino]-2-methyl-proprionitrile
2,4-D	2,4-Dichlorophenoxyacetic acid
DALAPON	2,2-Dichloropropionic acid
2,4-DB	4-(2,4-Dichlorophenoxy)butyric acid
DDE	Dichlorophenyl dichloro-ethylene (degradation product of DDT); *p,p′*-DDE: 1,1-Dichloro-2,2-bis(*p*-chlorophenyl) ethylene; *o,p′*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethylene
DDT	Main component (*p,p′*-DDT): α-Bis(*p*-chlorophenyl) β,β,β-trichloroethane. Other isomers are possible and some are present in the commercial product. *o,p′*-DDT: [1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane]
DESETHYL ATRAZINE	2-Chloro-4-amino-6-isopropylamino-1,3,5-triazine
DIAZINON	*O,O*-Diethyl *O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate
DICAMBA	3,6-Dichloro-*o*-anisic acid
DICHLORPROP	2-(2,4-Dichlorophenoxy)propionic acid
DIELDRIN	Not less than 85% of 1,2,3,4,10,10-Hexachloro-6,7,-epoxy-1,4,4a,5,6,7:8,8a-octahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene
DINOSEB	2-*sec*-Butyl-4,6-dinitrophenol
ENDOSULFAN	Hexachlorohexahydromethano-2,4,3-benzodioxathiepin 3-oxide
ENDRIN	Hexachloroepoxyoctahydro-*endo,endo*-dimethanonaphthalene
FENOPROP	2-(2,4,5-Trichlorophenoxy)propionic acid

(*Continued next page*)

APPENDIX (*Continued*)

HCB	Hexachlorobenzene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
LEPTOPHOS	*O*-(4-Bromo-2,5-dichlorophenyl) *O*-methyl phenylphosphonothioate
LINDANE	*Gamma* isomer of 1,2,3,4,5,6-hexachlorocyclohexane
LINURON	3-(3,4-Dichlorophenyl)-1-methoxy-1-methylurea
MALATHION	*O,O*-Dimethyl dithiophosphate of diethyl mercaptosuccinate
MCP	See MCPA
MCPA	2-Methyl-4-chlorophenoxyacetic acid
MECOPROP	2-(2-Methyl-4-chlorophenoxy)propionic acid
METHOXYCHLOR	2,2-Bis(*p*-methoxyphenyl)-1,1,1-trichloroethane 88% and related compounds 12%
METHYL PARATHION	*O,O*-Dimethyl *O*-*p*-nitrophenyl phosphorothioate
MIREX	Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene
OCTACHLOR EPOXIDE	1-*exo*-2-*endo*-4,5,6,7,8,8a-Octachloro-2,3-*exo*-*epoxy*-2,3,3a,7,7a-hexahydro-4,7-methanoindene
PARAQUAT	1,1′-Dimethyl-4,4′-bipyridilium ion (as dichloride salt)
PARATHION	*O,O*-Diethyl *O*-*p*-nitrophenyl phosphorothioate
PCA	Pentachloroaniline
PCBs (Polychlorinated Biphenyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
PCNB	Pentachloronitrobenzene
PCP	Pentachlorophenol
PEBULATE	*S*-Propyl butylethylthiocarbamate
PHOSVEL	See Leptophos
PICLORAM	4-Amino-3,5,6-trichloropicolinic acid
PROMETON	2,4-Bis(isopropylamino)-6-methoxy-*s*-triazine
RONNEL	*O,O*-Dimethyl *O*-(2,4,5-trichlorophenyl) phosphorothioate
SIMAZINE	2-Chloro-4,6-bis(ethylamino)-*s*-triazine
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
TCA	Trichloroacetic acid
TCNB	1,2,4,5-Tetrachloro-3-nitrobenzene
TDE	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorination products)
TERBUMETON	2-(*tert*-Butylamino)-4-(ethylamino)-6-methoxy-*s*-triazine
TERBUTHYLAZINE	2-(*tert*-Butylamino)-4-chloro-6-(ethylamino)-*s*-triazine
TOXAPHENE	Chlorinated camphene (67–69% chlorine). Product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating.
2,4,5-TP	2-(2,4,5-Trichlorophenoxy)propionic acid

The *Pesticides Monitoring Journal* welcomes from all sources qualified data and interpretative information on pesticide monitoring. The publication is distributed principally to scientists, technicians, and administrators associated with pesticide monitoring, research, and other programs concerned with pesticides in the environment. Other subscribers work in agriculture, chemical manufacturing, food processing, medicine, public health, and conservation.

Articles are grouped under seven headings. Five follow the basic environmental components of the National Pesticide Monitoring Program: Pesticide Residues in People; Pesticide Residues in Water; Pesticide Residues in Soil; Pesticide Residues in Food and Feed; and Pesticide Residues in Fish, Wildlife, and Estuaries. The sixth is a general heading; the seventh encompasses briefs.

Monitoring is defined here as the repeated sampling and analysis of environmental components to obtain reliable estimates of levels of pesticide residues and related compounds in these components and the changes in these levels with time. It can include the recording of residues at a given time and place, or the comparison of residues in different geographic areas. The Journal will publish results of such investigations and data on levels of pesticide residues in all portions of the environment in sufficient detail to permit interpretations and conclusions by author and reader alike. Such investigations should be specifically designed and planned for monitoring purposes. The Journal does not generally publish original research investigations on subjects such as pesticide analytical methods, pesticide metabolism, or field trials (studies in which pesticides are experimentally applied to a plot or field and pesticide residue depletion rates and movement within the treated plot or field are observed).

Authors are responsible for the accuracy and validity of their data and interpretations, including tables, charts, and references. Pesticides ordinarily should be identified by common or generic names approved by national or international scientific societies. Trade names are acceptable for compounds which have no common names. Structural chemical formulas should be used when appropriate. Accuracy, reliability, and limitations of sampling and analytical methods employed must be described thoroughly, indicating procedures and controls used, such as recovery experiments at appropriate levels, confirmatory tests, and application of internal standards and interlaboratory checks. The procedure employed should be described in detail. If reference is made to procedures in another paper, crucial points or modifications should be noted. Sensitivity of the method and limits of detection should be given, particularly when very low levels of pesticide residues are being reported. Specific note should be made regarding correction of data for percent recoveries. Numerical data, plot dimensions, and instrument measurements should be reported in metric units.

PREPARATION OF MANUSCRIPTS

——Prepare manuscripts in accord with the *CBE Style Manual*, third edition, Council of Biological Editors, Committee on Form and Style, American Institute of Biological Sciences, Washington, D.C., and/or the *U.S. Government Printing Office Style Manual*. For further enrichment in language and style, consult Strunk and White's *Elements of Style*, second edition, MacMillan Publishing Co., New York, N.Y., and *A Manual of Style*, twelfth edition, University of Chicago Press, Chicago, Ill.

——On the title page include authors' full names with affiliations and addresses footnoted; the senior author's name should appear first. Authors are those individuals who have actually written or made essential contributions to the manuscript and bear ultimate responsibility for its content. Use the Acknowledgment section at the end of the paper for crediting secondary contributors.

——Preface each manuscript with an informative abstract not to exceed 200 words. Construct this piece as an entity separate from the paper itself; it is potential material for domestic and foreign secondary publications concerned with the topic of study. Choose language that is succinct but not detailed, summarizing reasons for and results of the study, and mentioning significant trends. Bear in mind the literature searcher and his/her need for key words in scanning abstracts.

——Forward original manuscript and three copies by first-class mail in flat form: do not fold or roll.

——Type manuscripts on 8½-by-11-inch paper with generous margins on all sides, and end each page with a completed paragraph. Recycled paper is acceptable if it does not degrade the quality of reproduction. Double-space all copy, including tables and references, and number each page.

——Place tables, charts, and illustrations, properly titled, at the end of the article with notations in the text to show where they should be inserted. *Treat original artwork as irreplaceable material.* Lightly print author's name and illustration number with a ballpoint pen on the back of each figure. Wrap in cardboard to prevent mutilation; do not use paperclips or staples.

——Letter charts distinctly so that numbers and words will be legible when reduced. Execute drawings in

black ink on plain white paper. Submit original drawings or sharp glossy photographs: no copies will be accepted.

——Number literature citations in alphabetical order according to author. For journal article include, respectively, author, year, title, journal name as abbreviated in *Chemical Abstracts Service Source Index*, and volume, issue, and page numbers. For book references cite, respectively, author, year, chapter title, pages, and editor if pertinent, book title, and name and city of publisher. For Government manuals list originating agency and relevant subgroup, year, chapter title and editor if pertinent, manual title, and relevant volume, chapter, and/or page numbers. Do not list private communications among Literature Cited. Insert them parenthetically within the text, including author, date, and professional or university affiliation indicating author's area of expertise.

The Journal welcomes brief papers reporting monitoring data of a preliminary nature or studies of limited scope. A section entitled Briefs will be included as necessary to provide space for short papers which present timely and informative data. These papers must be limited to two published pages (850 words) and should conform to the format for regular papers accepted by the Journal.

Manuscripts require approval by the Editorial Advisory Board. When approved, the paper will be edited for clarity and style. Editors will make the minimum changes required to meet the needs of the general Journal audience, including international subscribers for whom English is a second language. Authors of accepted manuscripts will receive edited typescripts for approval before type is set. After publication, senior authors will receive 100 reprints.

Manuscripts are received and reviewed with the understanding that they have not been accepted previously for publication elsewhere. If a paper has been given or is intended for presentation at a meeting, or if a significant portion of its contents has been published or submitted for publication elsewhere, notations of such should be provided. Upon acceptance, the original manuscript and artwork become the property of the *Pesticides Monitoring Journal*.

Every volume of the Journal is available on microfilm. Requests for microfilm and correspondence on editorial matters should be addressed to:

Paul Fuschini (TS-793)
Editorial Manager
Pesticides Monitoring Journal
U.S. Environmental Protection Agency
Washington, D.C. 20460

For questions concerning GPO subscriptions and back issues write:

Superintendent of Documents
U.S. Government Printing Office
Washington, D.C. 20402

The Administrator of the U.S. Environmental Protection Agency has determined that the publication of this periodical is necessary in the transaction of public business required by law of this Agency. Use of funds for printing this publication approved by the Director of the Office of Management and Budget, May 19, 1976.

ORDER BLANK
FOR PMJ

To: Superintendent of Documents
Government Printing Office
Washington, D.C. 20402

Please enter my Subscription for Pesticides Monitoring Journal. I am enclosing Money Order ☐ Check ☐ for this subscription. ($7.90 a year; $2.00 additional for foreign mailing)

*Please address the PMJ as follows:*_____

_____

_____

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON, D. C. 1967

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D. C. 20402. Subscription price $7.90 a year, $2.00 additional for foreign mailing. Price for a single copy of this issue is $2.00.

United States
Environmental Protection
Agency
Washington DC 20460
TS-793

Postage and
Fees paid
Environmental
Protection
Agency
EPA 335

Official Business
Penalty for Private Use $300

Third-Class
Bulk Rate

If you do not desire to continue receiving this publication, please CHECK HERE ☐; cut off this label and return it to the above address. Your name will be removed from the mailing list.

3ERARP79031A 00168550000l 001
XEROX UNIV MICROFILMS
SERIALS DEPARTMENT
300 N ZEEB RD
ANN ARBOR MI 48106